Appendix D

Review of Groundwater Modeling and Monitoring

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This Appendix reviews mathematical modeling performed historically for the Monument Valley site and routine groundwater monitoring data for the alluvial aquifer. The modeling (1) produced quantitative estimates of alluvial aquifer properties and (2) evaluated several groundwater remedies that rely on aquifer pumping. Water chemistry data collected as part of routine monitoring are displayed in the form of contour maps of nitrate, ammonia, and sulfate concentrations. These maps, and graphs of contaminant concentrations at selected wells, are used to illustrate how the nitrate, ammonia, and sulfate plumes have changed during a 14-year period between the late 1990s and 2010. Possible causes of observed plume changes are also discussed. LM and Navajo Nation could use the historical groundwater monitoring data as a baseline for evaluating how well enhanced attenuation remedies, as reported herein, are working if implemented.

Historical computer modeling of groundwater flow at the Monument Valley site was performed to identify natural flow directions in the alluvial aquifer and to estimate the speed with which nitrate, ammonia and sulfate migrated from contaminant source areas in past years. Once flow directions and groundwater speeds were identified, additional computer modeling was conducted to simulate groundwater pumping remedies that might be implemented to clean up contaminants remaining in the aquifer. DOE had proposed pump-and-treat remedies before investigating enhanced natural attenuation remedies as alternatives (DOE 2000a).

Characterization of the site's hydrogeology and contamination in the alluvial aquifer was completed in 1997. Monitoring of groundwater levels and contaminant concentrations began shortly thereafter. The results of multiple years of groundwater sampling illustrate how ammonia, nitrate, and sulfate plumes have evolved in the alluvial aquifer since the late 1990s. Contour maps representative of contaminant plumes at different times over a 14-year period, and temporal plots of contaminant concentrations at several wells downgradient of the New Tailings Pile footprint, are used to demonstrate how source-area remediation and various phytoremediation tests have impacted contamination in the aquifer.

D.1 Modeling

Mathematical modeling of groundwater flow at contaminated sites is often performed for the purpose of better understanding how historical groundwater movement contributed to existing contaminant plumes. The modeling is very useful for estimating the values of aquifer properties that control the speed of migrating groundwater and for developing ways to clean up groundwater contamination. Once a reliable flow model has been developed, it is common for groundwater scientists to run the model many times in the interest of evaluating various groundwater remediation methods, such as groundwater pumping at specific wells. The model run of each groundwater remedy is an approximate prediction of how the contamination will be gradually removed from water in the subsurface.

Groundwater modeling at Monument Valley focused on the simulation of steady-state flow in the alluvial aquifer in areas located downgradient of former ore processing operations at the site. Several different conceptualizations of the groundwater system were tested with automated model calibration software before identifying a model that performed best in matching measured groundwater levels in the study area. The selected steady-state model was subsequently used in conjunction with computer-based optimization algorithms designed to identify efficient methods for cleaning up the alluvial aquifer. Application of these techniques to a variety of proposed groundwater remedies based on pump-and-treat technology resulted in the identification of an optimal remediation strategy.

D.1.1 Steady-State Flow

A steady-state flow model was developed for the alluvial aquifer at Monument Valley (DOE 2000b) using software developed and maintained by the U.S. Geological Survey (USGS). Sixteen different conceptual models were considered in the process of developing the steady-state flow model. Each conceptual model was calibrated using the USGS code MODFLOW (McDonald and Harbaugh 1988), a finite-difference simulator that can account for three-dimensional groundwater flow in heterogeneous domains, and using the automated parameter estimation techniques within the UCODE software (Poeter and Hill 1998). The steady-state flow model ultimately selected to represent groundwater flow in the alluvial aquifer at the site produced a reasonable match to observed groundwater levels at numerous wells monitored in the area north of the New Tailings Pile footprint.

All models considered in the UCODE analyses were two-dimensional with a single model layer of spatially variable thickness representing the alluvial aquifer. A spatially varied field of elevations representing the base of the alluvial aquifer (i.e., top of bedrock) was developed from available well construction information and adopted in the flow simulations. The model runs were conducted using version 3.50 of the graphical user interface called Groundwater Vistas (Environmental Simulations Inc. 1997), a Windows-driven package that contains graphical pre- and post-processors for MODFLOW models and facilitates easy data entry, data-file modification, program execution, and analysis of modeling results.

The final steady-state model assumed that hydraulic conductivity was spatially uniform (5.44 feet per day [ft/day]) throughout the aquifer and that all parts of the aquifer receives recharge at a constant rate of 3 inches per year. Five different ET zones, each with a distinct ET loss rate that depended largely on observed depth to groundwater, were employed in the model.

The selected model produced a steady-state flow field with an average horizontal, north-northeast gradient of about 0.0085 (dimensionless) and average linear velocities that generally averaged between 60 and 70 feet per year (ft/yr). Though the model performed well (DOE 2000b) in matching observed groundwater levels at numerous monitoring wells, observed lengths of the nitrate and sulfate plumes (approximately 4,500 feet [ft]) at the site in 1997 and 1998 indicated that the model-generated velocities were not large enough to have produced the plumes apparently caused by discharged process chemicals at the former mill site in the mid-1960s. A subsequent modeling effort conducted by Carroll and others (2009) that attempted to match observed nitrate concentrations in the alluvium at several different times between 1993 and 2007 showed results that inferred groundwater velocities on the order of 250 to 280 ft/yr occur in the aquifer. This in turn suggested that the hydraulic conductivity of 5.44 ft/day used throughout the DOE flow model was probably too low. The Carroll model (Carroll et al. 2009), which was based on aquifer testing results summarized in the SOWP, used a hydraulic conductivity of about 16 ft/day in the initial 2,000 ft of aquifer located downgradient of assumed nitrate sources in the vicinity of the New Tailings Pile, and a conductivity of about 25 ft/day beyond the 2,000-ft distance.

D.1.2 Early Groundwater Remedy Simulations

The SOWP (DOE 1999a) recommended that phytoremediation techniques, in conjunction with groundwater extraction and treatment, be used to remediate nitrogen-containing contaminants at the Monument Valley site. In the interest of designing an effective and efficient groundwater extraction system, the model ultimately selected to represent steady-state flow in the alluvial aquifer (DOE 2000b) was used to evaluate the relative merits of a variety of well-field configurations and pumping plans. This was accomplished with an optimization algorithm called the Brute Force method, as incorporated in the Groundwater Vistas (Environmental Simulations Inc. 1997) software package. The Brute Force technique combined groundwater flow simulations of a proposed pumping strategy with particle tracking to identify the flow paths and groundwater travel times that resulted from that strategy. The flow modeling was performed using MODFLOW and the particle tracking was conducted with the USGS package MODPATH (Pollock 1994). Optimization focused on maximizing the amount of contaminant mass removed while minimizing the number of wells needed to extract the mass, thereby minimizing overall groundwater remediation costs (DOE 2000c).

Two fundamentally different groundwater extraction strategies were considered in the optimization modeling runs: one that returns treated water to the aquifer (non-consumptive use) and one that does not (consumptive use). In addition to a single well field designed for pumping at a constant total rate for the duration of the cleanup action involved with each strategy, phased approaches were also evaluated with the strategies. The phased approach assumed that pumping would be concentrated in select locales during the first several years of remediation (Phase 1) for the purpose of removing contaminant hot spots, which was then followed with plume-wide groundwater extraction (Phase 2) to meet aquifer restoration goals within a specified time frame.

Three different well-field design alternatives were simulated under the non-consumptive use strategy. Each of these assumed that the groundwater would be pumped from vertical wells in the nitrate plume and that extracted groundwater would be returned to the alluvial aquifer at three upgradient locations, each representing a 250-ft long infiltration trench. Multiple model simulations, differing with respect to the duration of hot-spot removal and total remediation time, were conducted under the three alternatives. Subsequent analysis of the optimization modeling for the non-consumptive use strategy indicated that optimal aquifer remediation would be achieved through Phase 1 pumping for 5 years to remove hot spots followed by an additional 15 years of Phase 2 pumping from the nitrate plume as a whole.

Assessment of the consumptive use strategy also examined three different alternatives that varied according to duration of hot-spot removal and total remediation time (DOE 2000c). Though the exact processes leading to consumption of the pumped groundwater were not specified, use of the water to supply a spray evaporation system or support a land-farm phytoremediation operation were mentioned as possible candidates. Ultimately, an optimal remedy was identified that called for 5 years of hot-spot removal followed by 20 years of plume-wide groundwater extraction, a solution that was similar to the recommended alternative under the non-consumptive use strategy.

Though the various active remediation designs considered in the modeling (DOE 2000c) helped to identify optimal pumping alternatives, no attempt has since been made to pursue pump-and-treat methods for aquifer cleanup. Alternatively, the purpose of this report is to recommend a groundwater remediation approach that utilizes either natural or enhanced attenuation processes, or some combination thereof.

D.2 Monitoring

Before and after the mathematical modeling, groundwater elevations and the concentrations of contaminants in the groundwater were measured. The collection of water-level and concentration data at regular time intervals during the months and years after model predictions have been made is called groundwater monitoring, and the data collected during each monitoring event provides a snapshot of how aquifer cleanup is progressing. By comparing individual snapshots with model predictions of aquifer remediation, groundwater scientists can determine whether the remedy is working as expected. If the aquifer is not cleaning up as fast as predicted, scientists may decide to modify the groundwater remedy or select a new one.

Extensive site characterization work was conducted in 1997 to develop a comprehensive understanding of groundwater flow and transport processes at the site. This work involved geophysical surveys, the drilling and logging of multiple wells, water-level measurements, and groundwater sampling and analysis. Prior to finalization of the SOWP (DOE 1999a), additional groundwater chemistry data were collected as a result of two sampling events in 1998. The 1998 data collection effort served not only to further describe natural groundwater chemistry in the vicinity of the site but also to confirm the lengths of the ammonia, nitrate, and sulfate plumes in the alluvial aquifer and the concentrations of these constituents in their respective plumes, particularly along each plume's longitudinal axis. The axes of the plumes appeared to be collinear, indicating that all three plumes originated in the vicinity of the New Tailings Pile footprint.

Groundwater monitoring has been conducted routinely at the Monument Valley site since 1997, with sampling occurring once a year in some years and twice during others. The results of sampling in 1997 and 1998 can be used to describe starting configurations for contaminant plumes that have evolved in the alluvial aquifer through 2010. The following report sections discuss the degree to which the plumes of ammonia, nitrate, and sulfate have changed, if at all, during that time period. Possible reasons for the observed changes are given in the interest of developing a more thorough understanding of contaminant fate at the site.

D.2.1 Ammonia

The disposition of the ammonia plume can be approximately discerned by examining contour maps of ammonia as nitrogen (NH_3[N]) concentration in 1997 and 1998 (Figure D–1), June 2007 (Figure D–2) and December 2010 (Figure D–3). These three figures imply that the northern extent of the ammonia plume over a period of 14 years has remained about 3,000 ft north of the New Tailings Pile footprint, far short of 4,500 plume lengths that have been ascribed to nitrate and sulfate plumes north of the New Tailings Pile footprint. Comparison of the 1997–1998 and 2010 plume maps suggests that ammonia concentrations at five wells in and near the plume core (606, 655, 656, 770, 771) decreased steadily by as much 10 to 50 percent between these two times. Whereas this is basically true for wells 606, 656, and 770, a temporal plot of ammonia concentrations at several site wells between 1997 and 2010 (Figure D–4) shows that consistently decreasing concentrations were not observed at wells 655 and 771. Though NH_3-N levels at these two co-located wells fluctuated greatly from 1997 through 2010, no discernible, steadily decreasing trends in concentration were observed in the water samples collected from them.

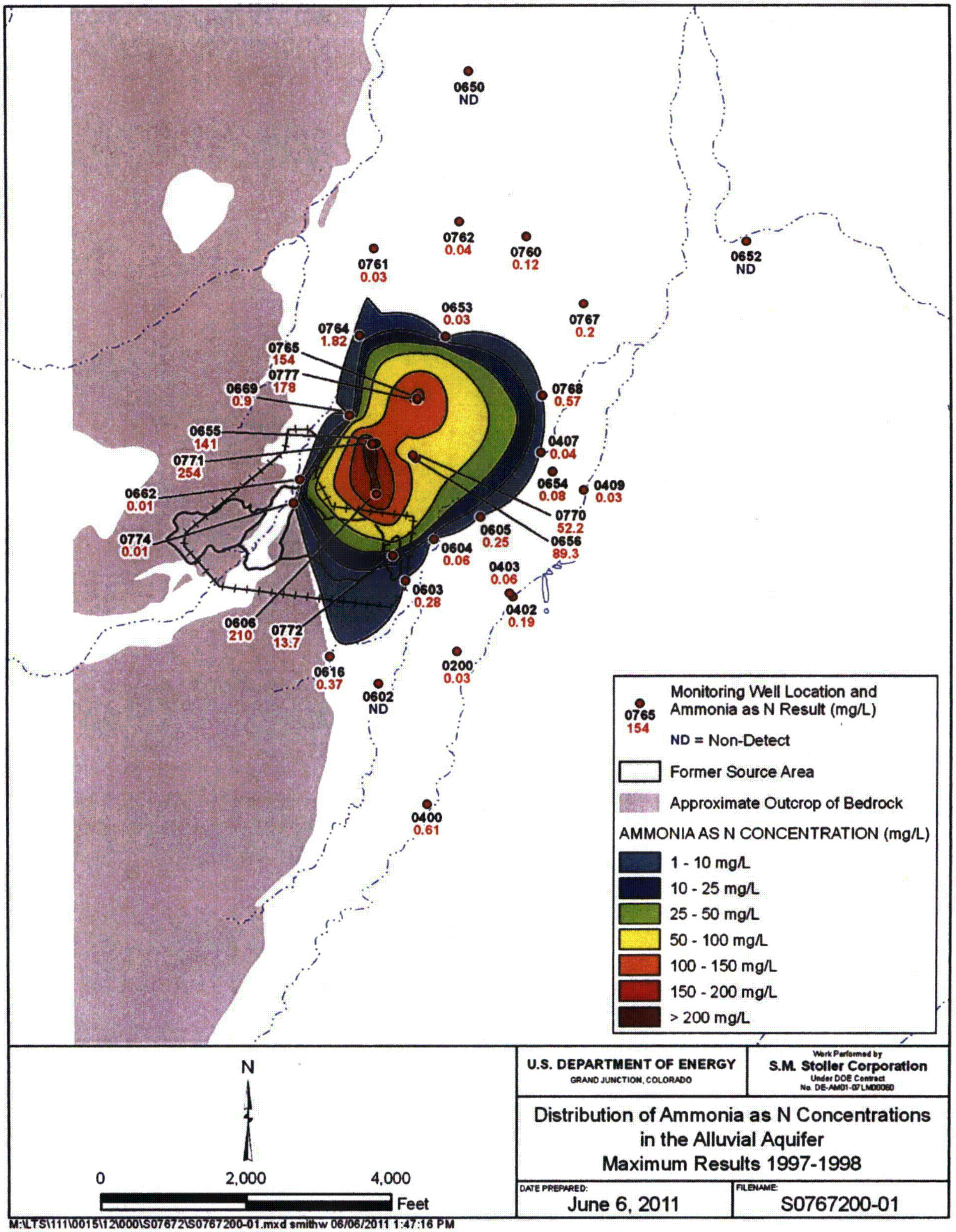

Figure D–1. Distribution of maximum ammonia (as N) concentrations during 1997 and 1998.

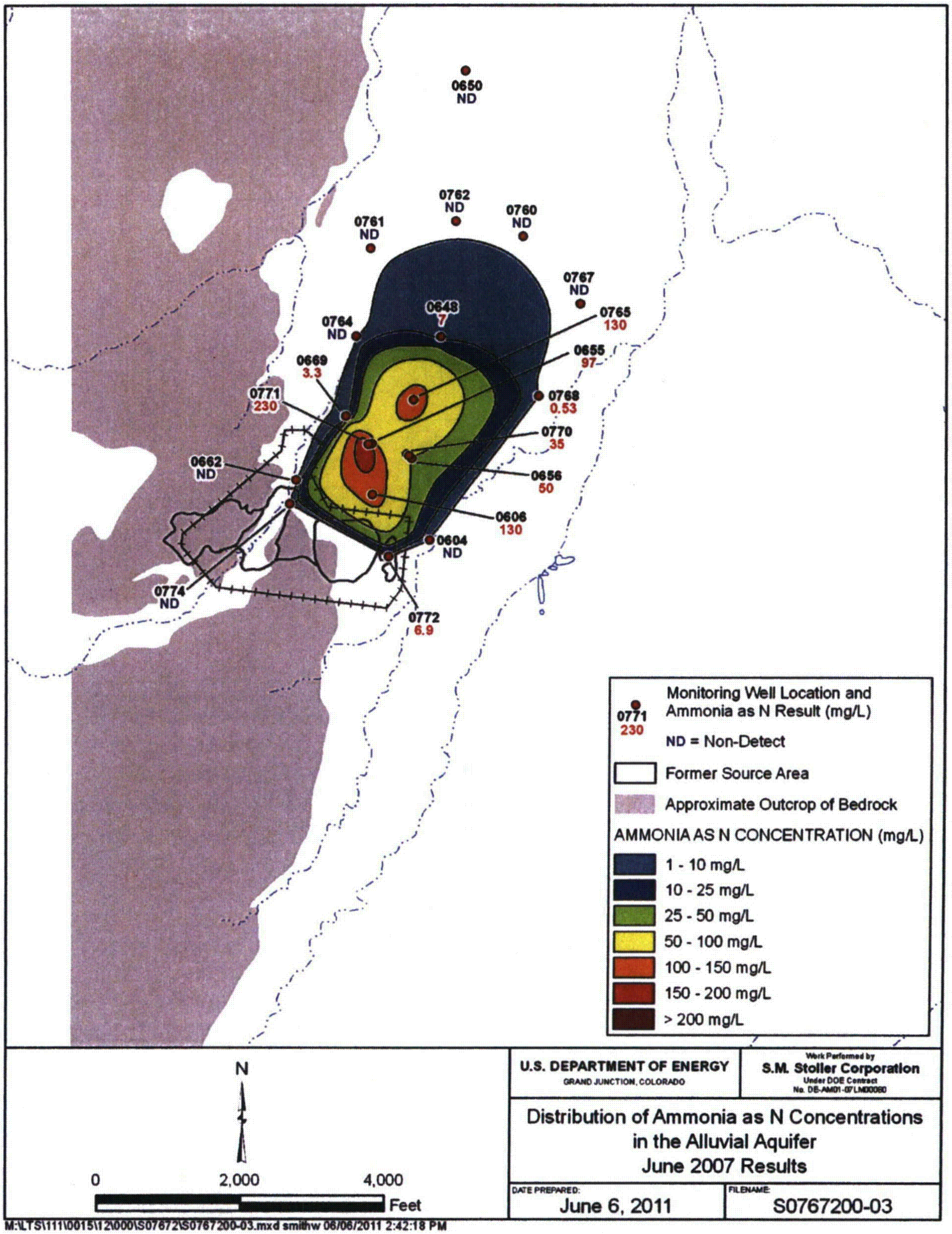

Figure D–2. Distribution of ammonia (as N) concentrations in June 2007.

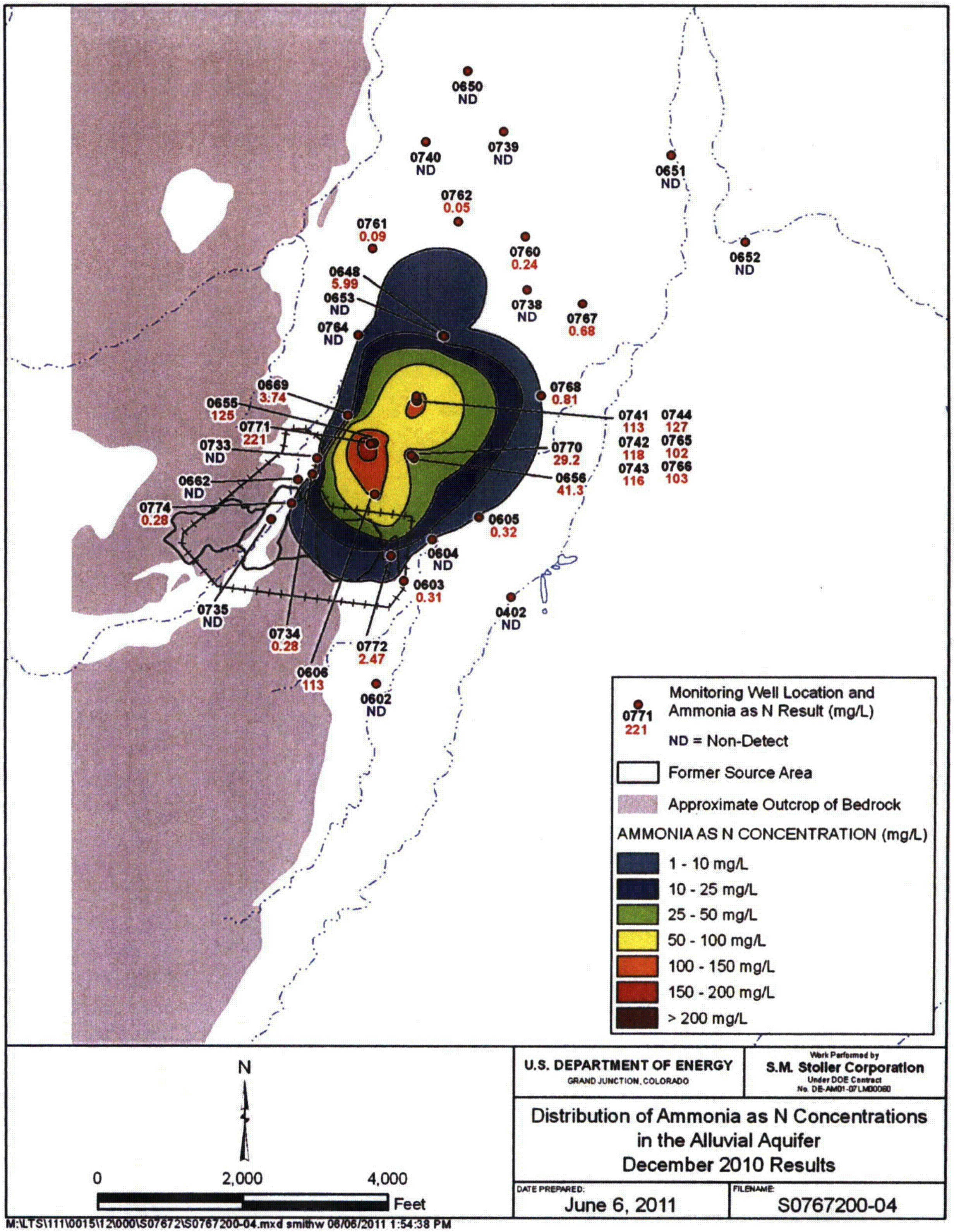

Figure D–3. Distribution of ammonia (as N) concentrations in December 2010.

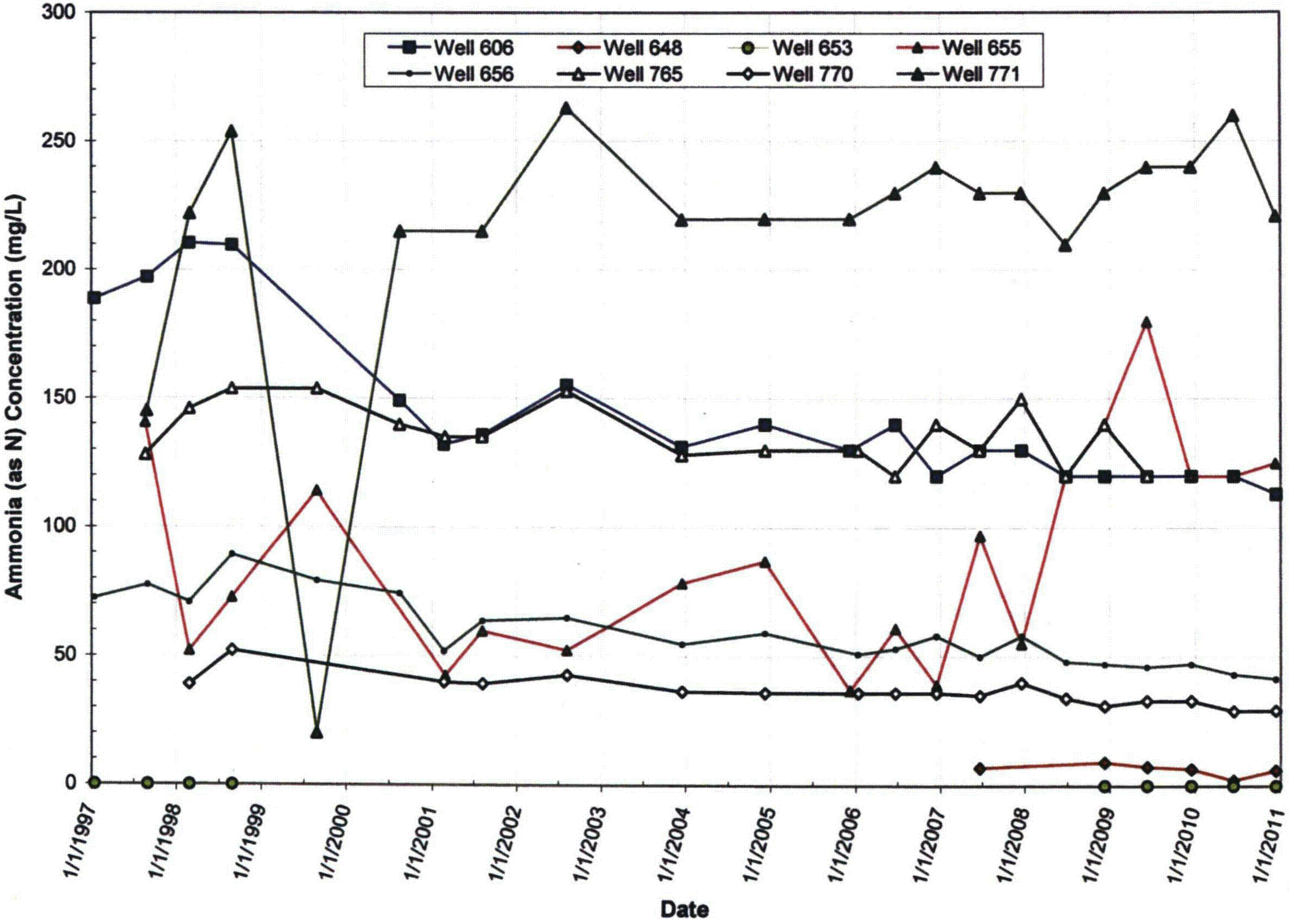

Figure D–4. Ammonia (as N) concentrations along and near the plume axis from 1997 to 2010.

Well 606 lies in the center of a 50 m by 50 m square plot that was used for phytoremediation testing. Fourwing saltbush were planted in the test plot in 2005, and the plants gradually reached a healthy, mature state. Hence, the decrease in ammonia concentration by about half at this location between 1997–1998 and 2010 (210 to 113 mg/L $NH_3[N]$) is probably attributable to ammonia uptake by the roots of this phreatophyte planting. Though it is also possible that the recharge irrigation water applied to the test plot during the first few years of the phytoremediation testing helped to dilute underlying groundwater, subsurface monitoring in the test plot indicated that deep migration of the applied water during and shortly after the irrigation period was limited. Consequently, dilution was unlikely to have impacted ammonia levels in well 606 to the degree shown in Figure D–4.

Similar decreases in ammonia concentration by about half at wells 656 and 770 between 1997–1998 and 2010 were also probably the result of a phytoremediation pilot study. These two wells are in the center of a mature stand of black greasewood that was historically overgrazed. Since about 2000, the stand has recovered as the grazing pressure declined to become a healthy population that has the capacity to remove ammonia via root uptake.

The low NH_3-N concentrations seen consistently at co-located wells 648 and 653 (Figure D–4), which are at the leading edge of the ammonia plume, indicate the plume is not progressing farther to the north. Historical ammonia concentrations at well 765, located approximately 900 ft south of wells 648 and 653, provide further evidence that the plume is not migrating northward. Despite the fact that NH_3-N levels at this well were consistently high (>100 mg/L) between 1997–1998 and 2010, the concentrations remained relatively constant and showed no signs that they were steadily increasing. Note that concentration data for well 765 beyond early 2009 are omitted from Figure D–4 because a push-pull test of enhanced attenuation conducted in the well in the second half of 2009 impacted local contaminant concentrations.

Ammonia concentrations in groundwater samples from co-located wells 655 and 771 from 1997–1998 through 2010 (Figure D–4) are of particular interest because of the sizable differences in concentration typically observed between them. Though the wells were installed about 50 ft from each other, NH_3-N levels at well 771 have commonly been 2 to 3 times the comparable concentrations observed at well 655. Possible reasons for the disparity in ammonia concentration can be surmised by examining the well logs for the respective wells. These indicate that each well is screened over a 20 ft vertical interval, the midpoint elevation of the screen in well 771 is 27.5 ft lower than the midpoint elevation of the well 665 screen, and overlap of the two screened intervals is limited to 2.5 ft. In addition, the geologic log for the deeper well (771) indicates the possible presence of fine-grained materials, particularly clay, in the bottom 10 ft of the well borehole, whereas no such fine-grained sediment is observed in the shallower well. These observations suggest that ammonia concentrations have the potential to vary noticeably with depth in the aquifer, with concentrations in this part of the plume increasing with depth. However, it also possible that aquifer heterogeneity is primarily responsible for the disparate concentrations, such that the clay apparently present in a deeper horizons at well 771 is somehow related to higher ammonia levels.

The potential for contaminant concentrations to vary noticeably over short distances in the aquifer can be further analyzed by examining NH_3-N levels in co-located wells 656 and 770 between 1997–1998 and 2010 (Figure D–4). These two latter wells are also located about 50 ft from each other and the screened interval in well 770 is deeper than that in well 656. Vertical separation between the screened intervals for the wells is less dramatic than at the well 655/771 pair, as the midpoint elevations for the respective screens differ by 11 ft and screen overlap is 4 ft. In addition, neither of the geologic logs for the two locations indicates the presence of clayey material. The ammonia concentrations in the two wells tend to be close in magnitude, with the shallower well (656) during recent years consistently exhibiting NH_3-N concentrations that are about 30 percent larger than equivalent concentrations in the deeper well (770). Obviously, the larger concentrations observed in the shallower well contradicts the notion that concentrations tend to increase with depth. As previously discussed, wells 656 and 770 are located in a phytoremediation test plot, but it is unclear whether apparent root uptake of ammonia associated with the testing played a role in creating larger NH_3-N levels at the shallower vertical interval in the aquifer.

Though it is clear that dissolved ammonia concentrations can vary significantly over relatively short distances of tens of feet, the limited data presented above for the two sets of co-located wells (wells 655 and 771, wells 656 and 770) are inadequate for deciphering all factors influencing ammonia levels in a local area. Nevertheless, the fact that NH_3-N concentrations at one well location can be as much as 2 to 3 times the value of comparable concentrations in a well as little as 50 ft away implies that aquifer heterogeneity has the potential to strongly influence spatial distributions of contaminants in site groundwater. Accordingly, the possibility that local contaminant migration mostly occurs within preferential flow paths (i.e., zones of higher hydraulic conductivity; Zheng and Gorelick 2003) cannot be discounted.

D.2.2 Nitrate

Plume maps displaying nitrate as nitrogen (NO_3[N]) concentrations at the site in 1997–1998, 2000, 2007, and 2010 are presented in Figures D–5, D–6, D–7, and D–8, respectively. An obvious progression observed in nitrate distribution over this time period is an extension of the plume to the north, manifested by a gradual increase in concentration at well 762, located near the plume's leading edge, about 4,500 ft north of the New Tailings Pile footprint. As shown in the plume maps, NO_3-N concentrations at this location appeared to increase steadily from about 17 mg/L in 1997–1998 to greater than 95 mg/L in December 2010. A temporal plot of nitrate levels at wells along and near the plume axis (Figure D–9) reveals that nitrate increased in concentration at well 762 between 1997 and late 2008 (~130 mg/L), and subsequently decreased to a constant concentration of about 100 mg/L thereafter. A slight but steady increase in NO_3-N concentration at well 650 from less than 0.3 mg/L in 1997 to greater than 2 mg/L in 2010 also suggests that the leading edge of the nitrate plume migrated farther north during the 14-year monitoring period.

Co-located wells 655 and 771 also experienced discernible upward trends in nitrate concentration from the late 1990s through 2010 (Figures D–5 through D–8), with both wells exhibiting increases in NO_3-N level on the order of 40 to 50 mg/L since 1998 (Figure D–9). The reason for the gradual rise in concentration in the vicinity of these wells is unknown. Note that the disparity in NO_3-N concentration at wells 655 and 771 during the monitoring period was far less than comparable differences observed for ammonia (Figure D–4). Nonetheless, as in the case of ammonia, the larger nitrate concentrations were typically observed in well 771 (Figure D–9), which is screened at a greater depth than well 655.

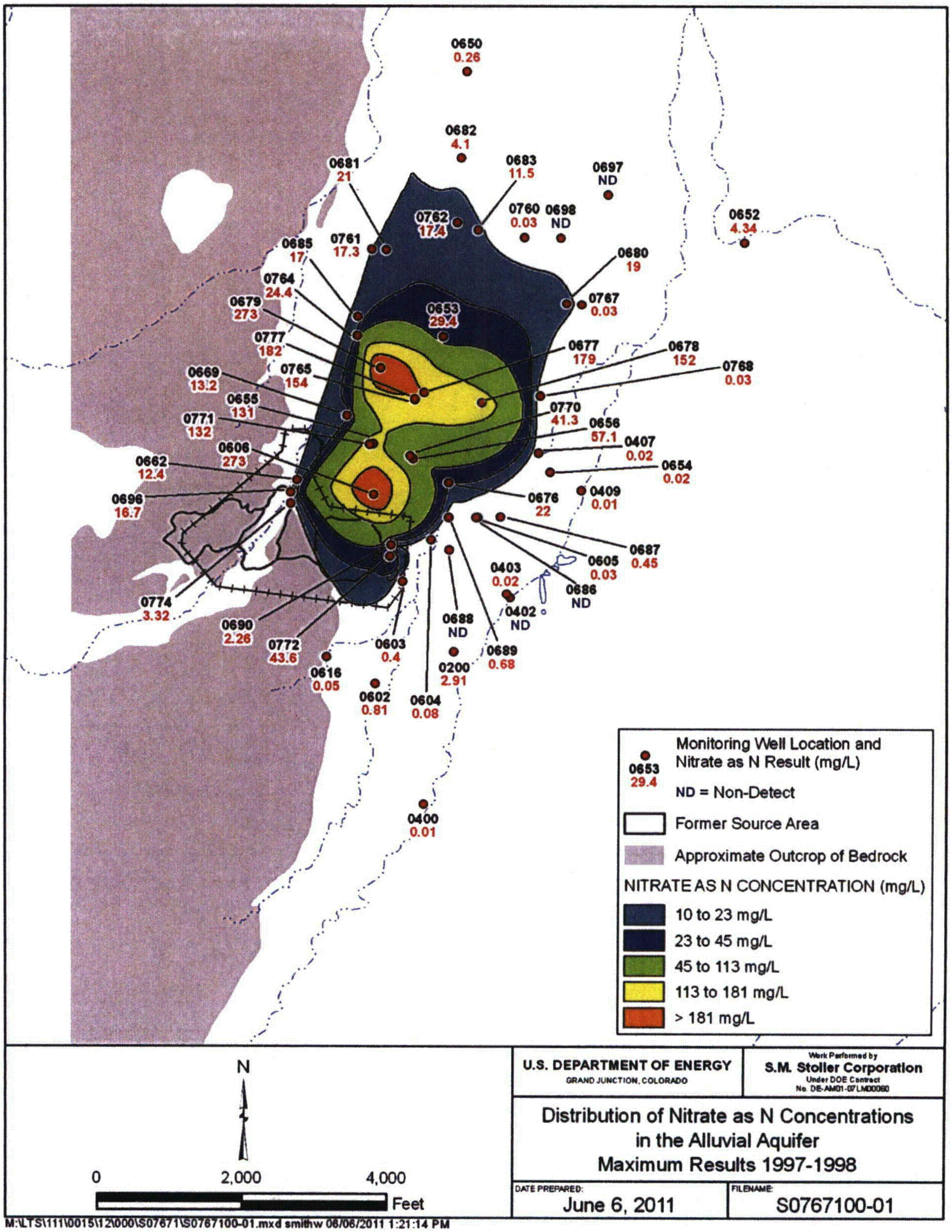

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Figure D–5. Distribution of maximum nitrate (as N) concentrations in the alluvial aquifer during 1997 and 1998.

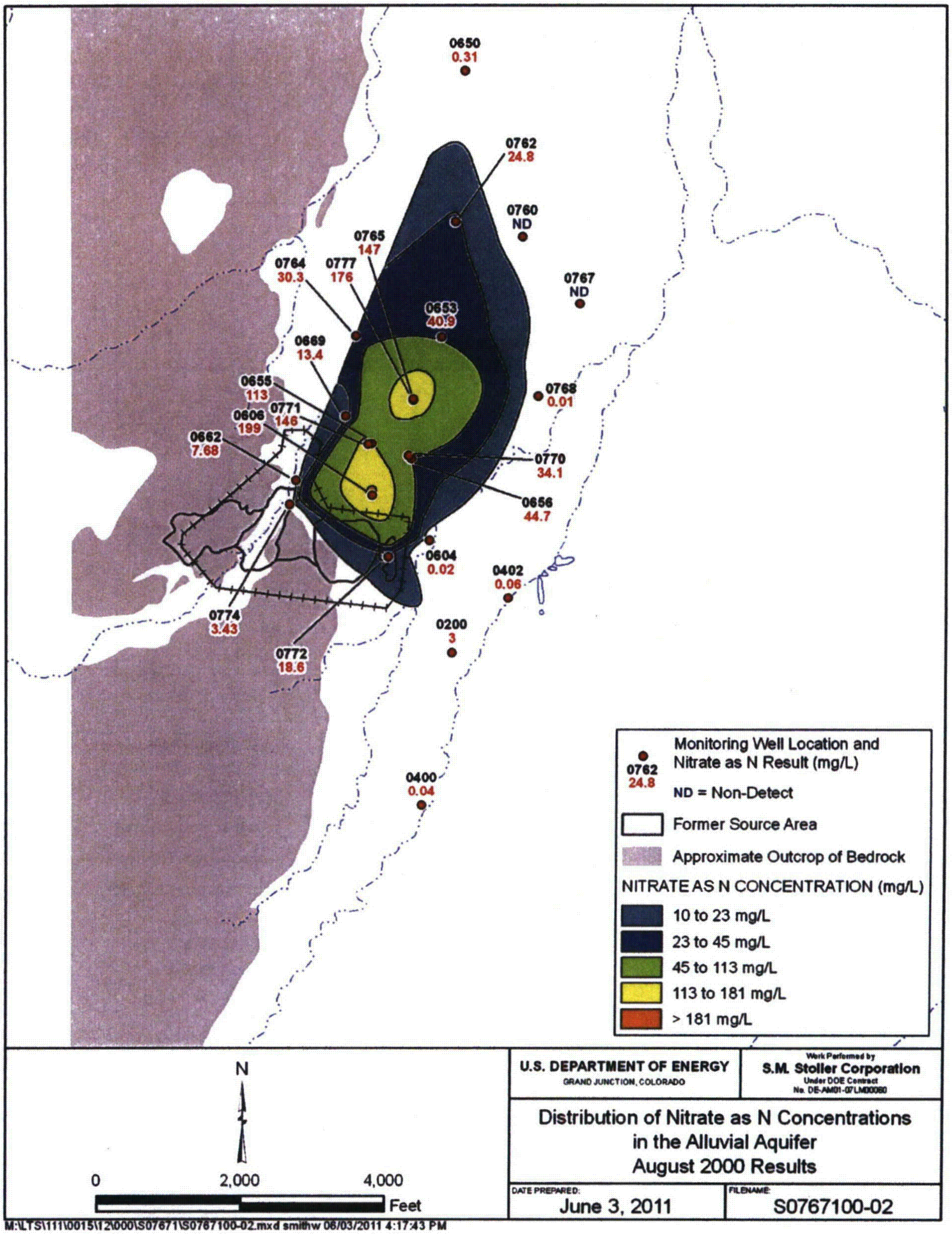

Figure D–6. Distribution of nitrate (as N) concentrations in the alluvial aquifer in August 2000.

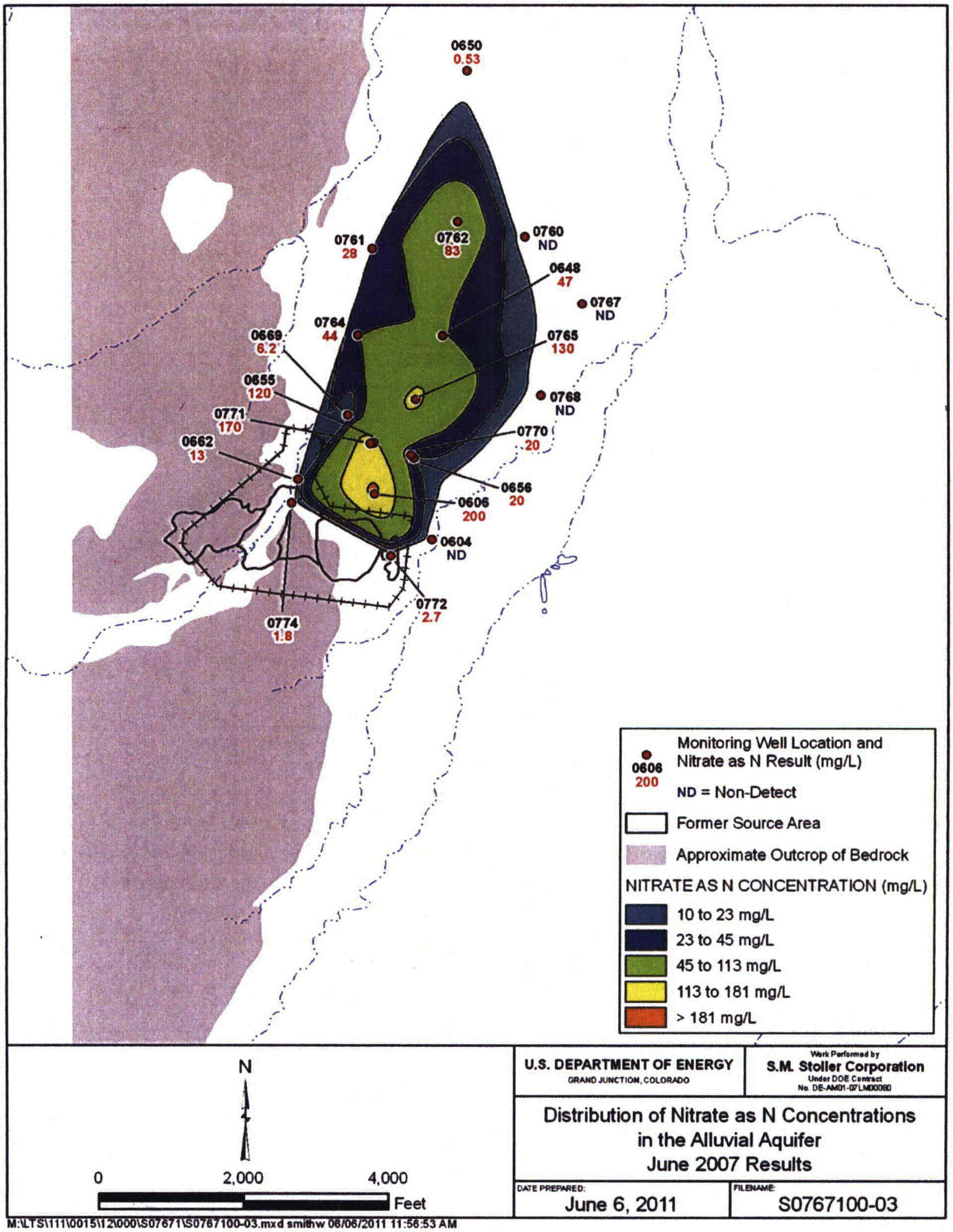

Figure D–7. Distribution of nitrate (as N) concentrations in June 2007.

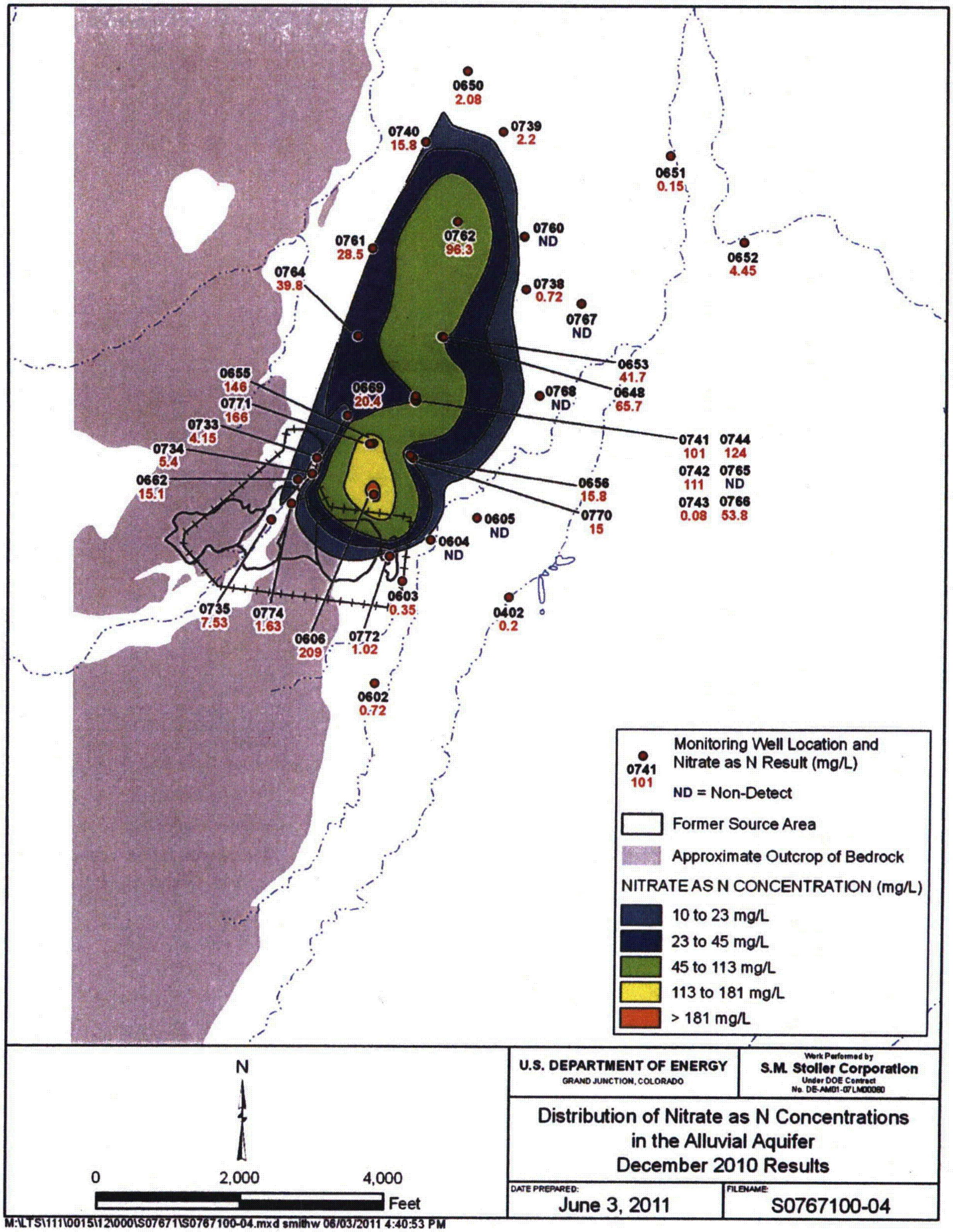

Figure D–8. Distribution of nitrate (as N) concentrations in December 2010.

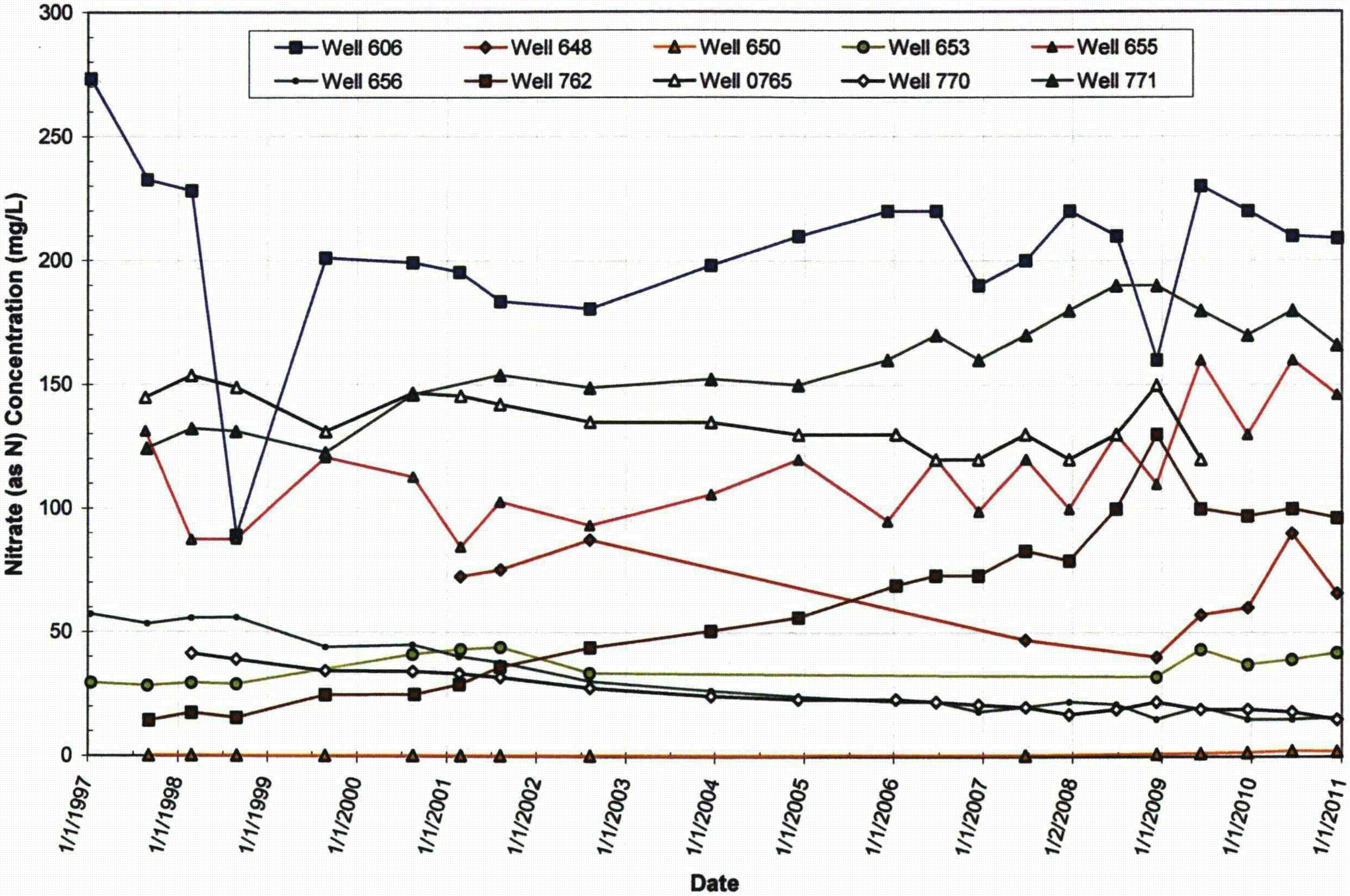

Figure D–9. Nitrate (as N) concentrations along and near the plume axis from 1997 to 2010.

In contrast to ammonia behavior, nitrate levels during 14 years of monitoring at well 606 did not show a clear decreasing trend. Rather, NO_3-N concentrations at this well mostly remained above 200 mg/L since 1997 (Figure D–9), despite fluctuating significantly. This observation indicates that attempts at phytoremediation in the test plot surrounding well 606 had no discernible impact on local nitrate contamination.

As indicated by the temporal plot of NO_3-N concentrations (Figure D–9), co-located wells 648 and 653 tended to exhibit relatively constant nitrate levels during the years that they were monitored. Because these wells lie about 800 ft hydraulically upgradient of well 762, which is representative of the nitrate plume's leading edge, the relatively stable concentrations in each suggest that, during the 14 years of monitoring, nitrate was feeding into the local portion of the plume at the same rate that it was migrating farther to the north. Nitrate in wells 648 and 653 was also of interest because the wells are only 16 ft apart and the midpoint elevations of their screened intervals are within 5 ft of each other, yet nitrate levels in the former were consistently 10 to 50 mg/L larger than comparable concentrations in the latter. This observation supported a previous observation that contaminant concentrations have the potential to vary significantly over short distances in the alluvial aquifer. Again, the data provide evidence for the presence of preferential flow paths.

Similar to observed nitrate in wells 648 and 653, NO_3-N concentrations in well 765 remained relatively constant between 1997–1998 and 2010 (see Figures D–5 through D–9), providing evidence of a balance between nitrate influx and efflux in the portion of the plume sampled by this well. As in the case of ammonia, NO_3-N concentration data collected at well 765 after the first half of 2009 were omitted from Figure D–9because a push-pull test of enhanced attenuation conducted at this location in the second half of 2009 impacted local contaminant concentrations. The plume map in Figure D–8shows that the enhanced attenuation testing had reduced nitrate to non-detect levels at well 765 as of 2010.

In contrast to the consistently different ammonia concentrations measured at co-located wells 656 and 770 (Figure D–4), NO_3-N levels in these two wells remained very close in magnitude during the 13 years between 1998 and 2010 (Figure D–9). The difference in ammonia concentration between the two locations averaged about 10 mg/L from early 1998 through early 2001, but differences in subsequent years tended to remain within about 3 mg/L. Though it is difficult to find a reason for differing ammonia concentrations between the neighboring wells when comparable nitrate levels were very similar, it is possible that variable impacts of phytoremediation testing in the vicinity of the wells contributed to this apparent paradox. Regardless of the cause of the contradictory observations regarding ammonia and nitrate, gradually decreasing NO_3-N concentrations at both wells 656 and 770 between 1997–1998 and 2010 (Figures D–5 through D–9) suggests that the phytoremediation testing was helping to attenuate local nitrate levels.

Comparison of the NO_3-N plume contours for 1997–1998 conditions (Figure D–5) with subsequent plume maps in 2000, 2007, and 2010 (Figures D–6 through D–8) suggests that the nitrate plume was wider during the start of the 14-year monitoring period than it was in later years. This observation stems from the fact that the isopleths plotted in the 1997–1998 map made use of nitrate concentrations measured in June 1997 at well 678, a hydro-punch well that was abandoned shortly after it was first drilled. Thus, without the benefit of subsequently measured concentrations at this location, the plume contours representing conditions in 2000, 2007, and 2010 implied a narrower plume. Additional nitrate concentrations from sampling locations east of well 678 (wells 768 and 767) have never yielded data that are indicative of a plume that expands farther to the east than shown in Figures D–6 through D–8.

The observed tendency of concentrations at wells along and near the nitrate-plume axis (606, 655, 771, 765, 648, 653) to either remain relatively constant or increase over the 14-year monitoring period suggests that biologically mediated denitrification in the alluvial aquifer, if it is occurring, is mildly impacting the plume core. It is possible, however, that denitrification may take place along the east and west edges of the nitrate plume, where mixing of dissolved organic carbon in the aquifer with electron acceptors is potentially enhanced.

D.2.3 Sulfate

Of the three contaminants that impact the alluvial aquifer, sulfate showed the greatest tendency to attenuate in groundwater during the 14-year monitoring period. This tendency was seen primarily in wells located in the southern half of the sulfate plume, as shown in the succession of plume maps for 1997–1998 (Figure D–10), 2000 (Figure D–11), 2007 (Figure D–12) and 2010 (Figure D–13). As illustrated in a temporal plot of sulfate concentrations (Figure D–14), five of the monitoring wells in the southern half of the plume (606, 653, 656, 770, 765) experienced gradual, and mostly steady, decreases in sulfate concentration. Using the starting and ending concentrations presented in Figure D–14, the calculated drop in concentration at these wells fell in the range of 40 to 55 percent. These findings strongly suggest that the source of the sulfate was greatly reduced, if not terminated, at some time in the early 2000s. Phytoremediation in the source area has greatly limited percolation and may have curtailed deep percolation of sulfate once the plants matured (Appendix B, Section B.3). Therefore, it is logical to assume that source area remediation is responsible for much, if not all, of the sulfate attenuation in the southern half of the plume.

The greatest decrease in sulfate mass was observed at well 771, where sulfate levels were higher than 3,500 mg/L in 1997 and 1998, but had been reduced to less than 1,500 mg/L in December 2010 (Figure D–14). This large decline in concentration contrasts with the behavior of sulfate in co-located well 655, which generally maintained sulfate levels that fluctuated between 1,500 and 2,000 mg/L from 1997 to late 2007, and subsequently decreased to about 1,000 mg/L in late 2010. As a result of this behavior, sulfate concentrations in wells 656 and 771 tended to remain close in magnitude between 2005 and 2010. Though it is difficult to pinpoint why sulfate levels differed greatly between the two wells at the start of the 14-year monitoring period yet approximated each other at a later time, it is likely that the previously discussed vertical offset of screened intervals in the respective wells (Section B.2.1) and the apparent presence of clay near the bottom of the deeper well (771) helped play a role.

Well 648, co-located with well 653, showed a clear decrease in sulfate concentration from about 1,700 mg/L in 2001 to about 900 mg/L in 2007, and remained slightly below 1,000 mg/L through 2010. During sampling events when both of the co-located wells were sampled, their sulfate concentrations tended to stay close in value, generally differing by no more than 200 mg/L. Nevertheless, the frequent difference in observed concentration between two locations separated by 16 ft confirmed the potential for contaminant levels to vary significantly over very small distances.

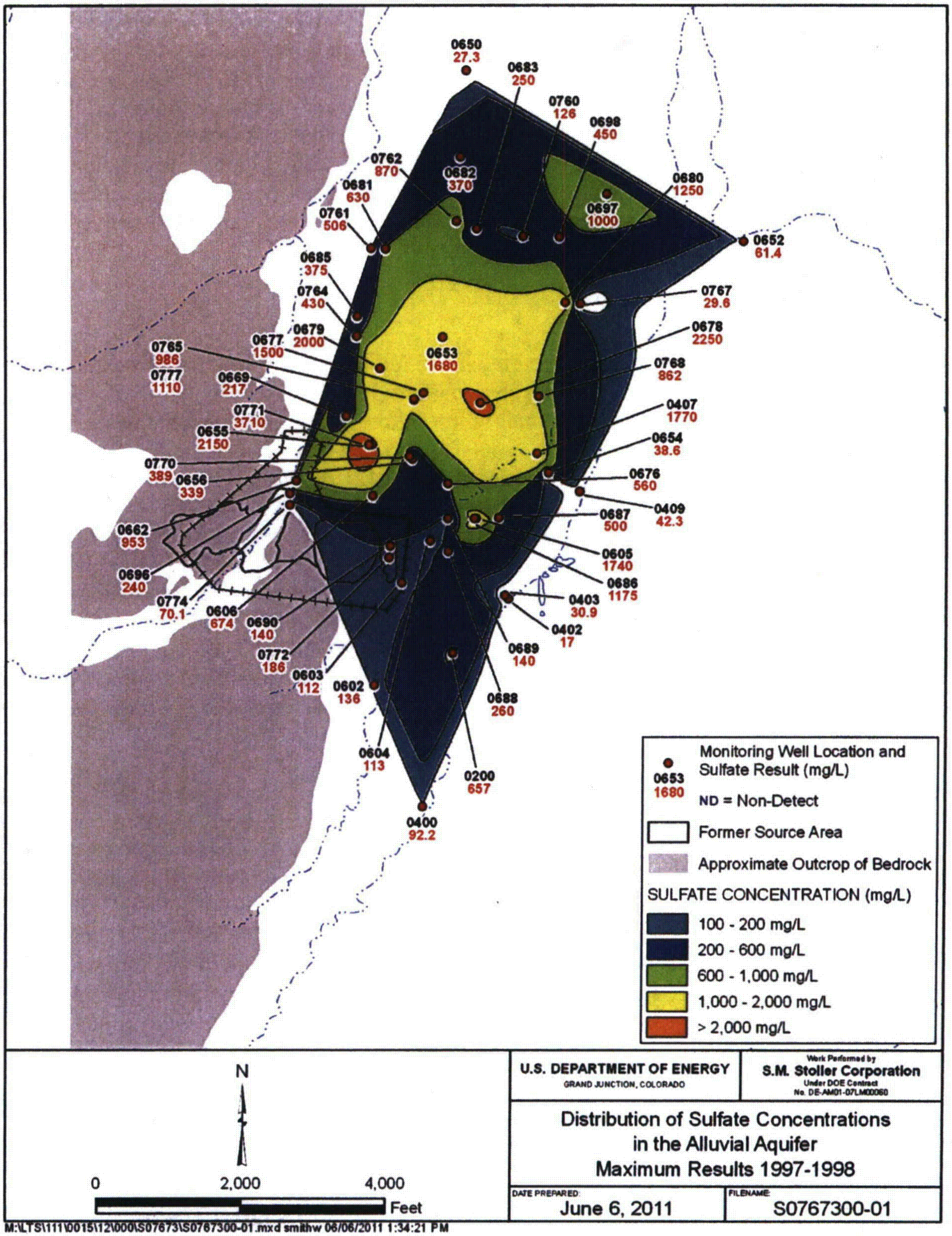

Figure D–10. Distribution of maximum sulfate concentrations during 1997 and 1998.

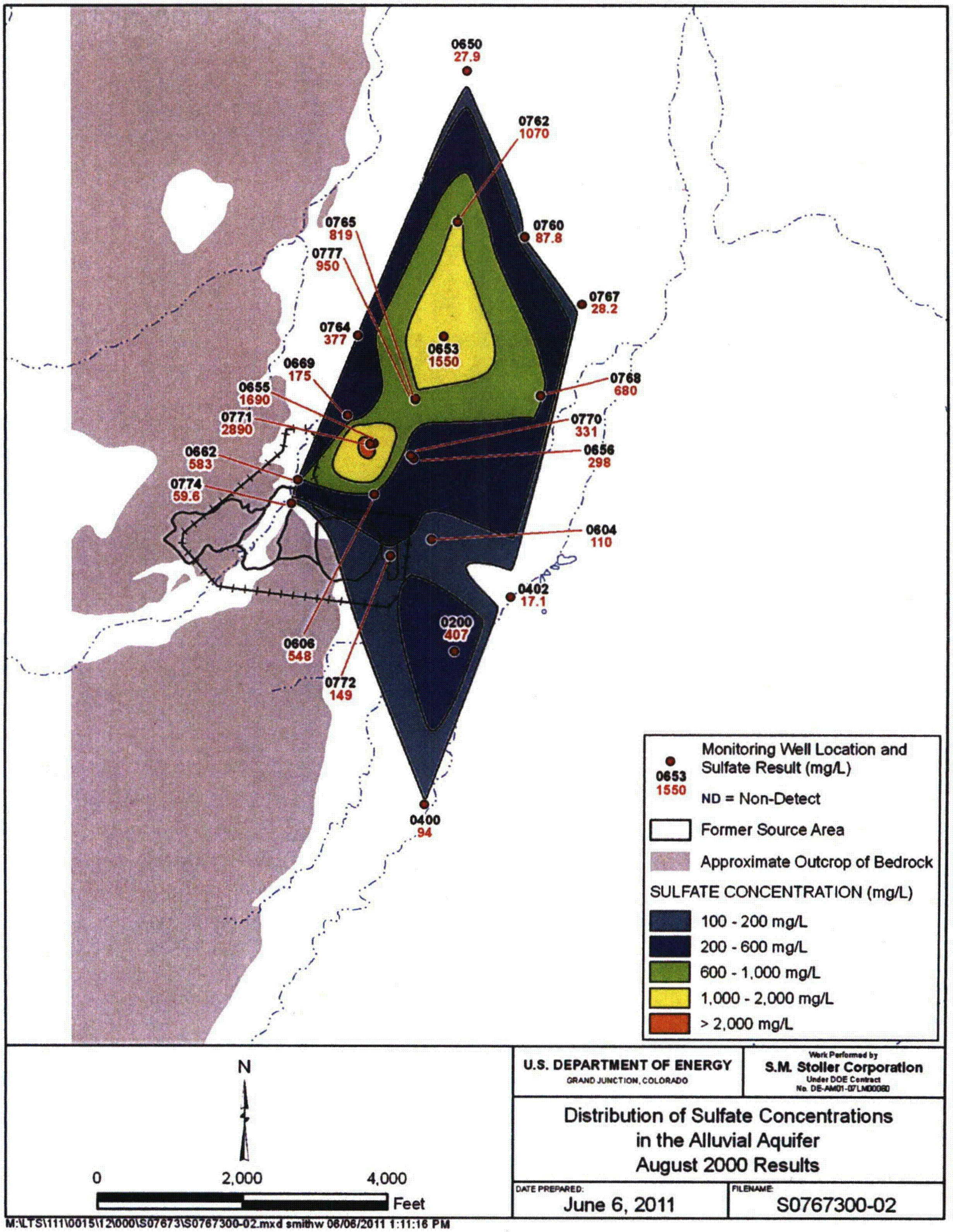

Figure D–11. Distribution of sulfate concentrations in August 2000.

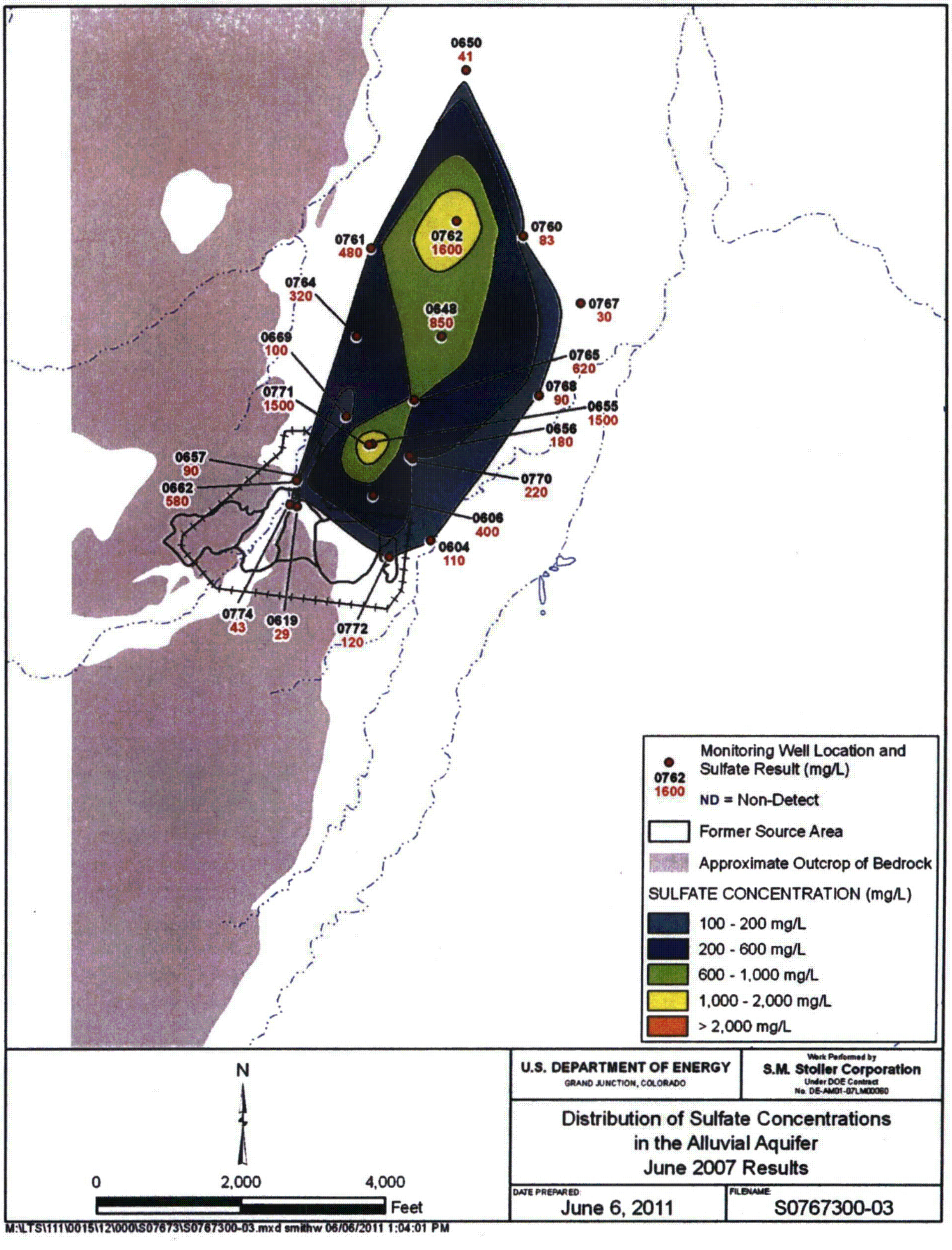

Figure D–12. Distribution of sulfate concentrations in June 2007.

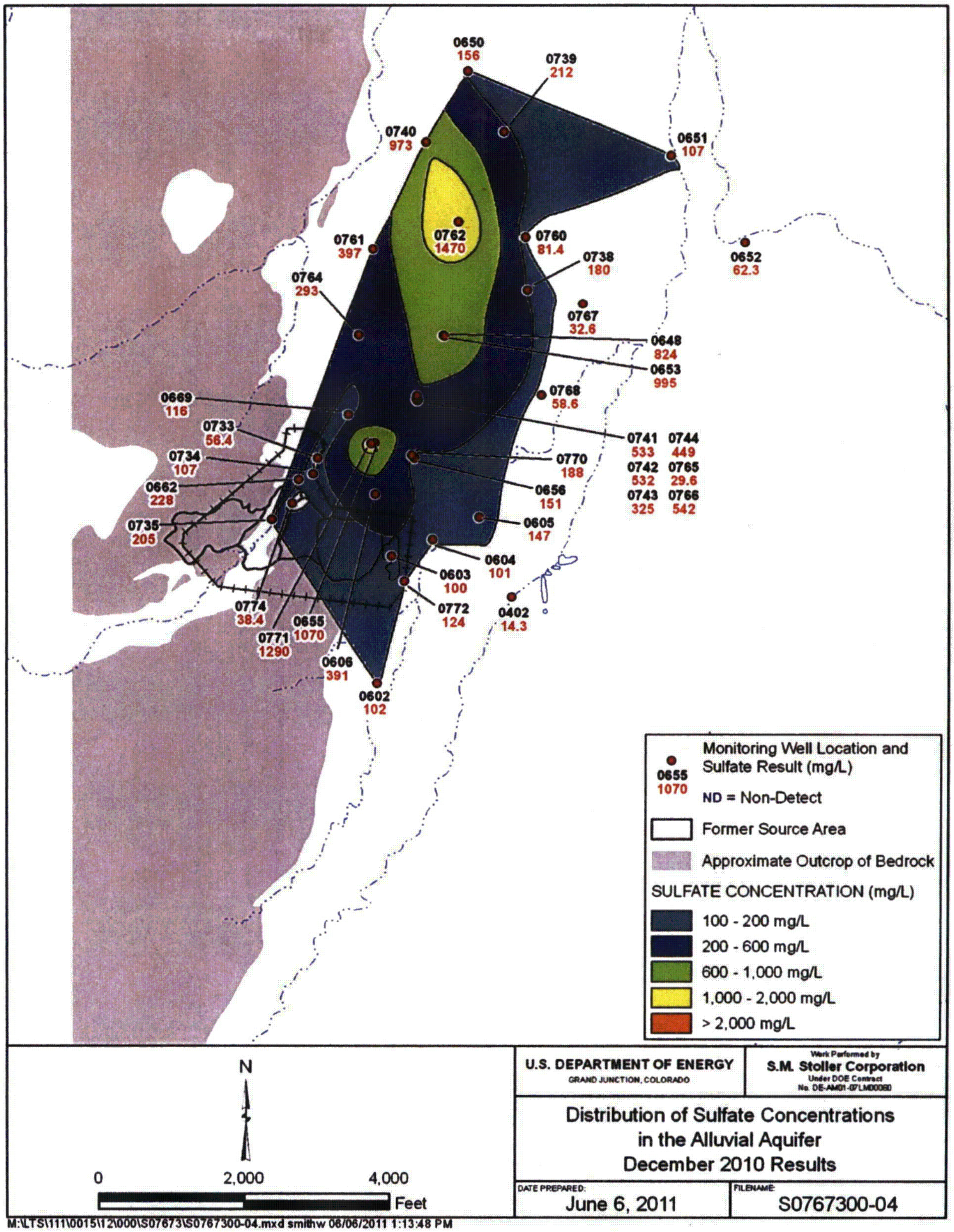

Figure D–13. Distribution of sulfate concentrations in December 2010.

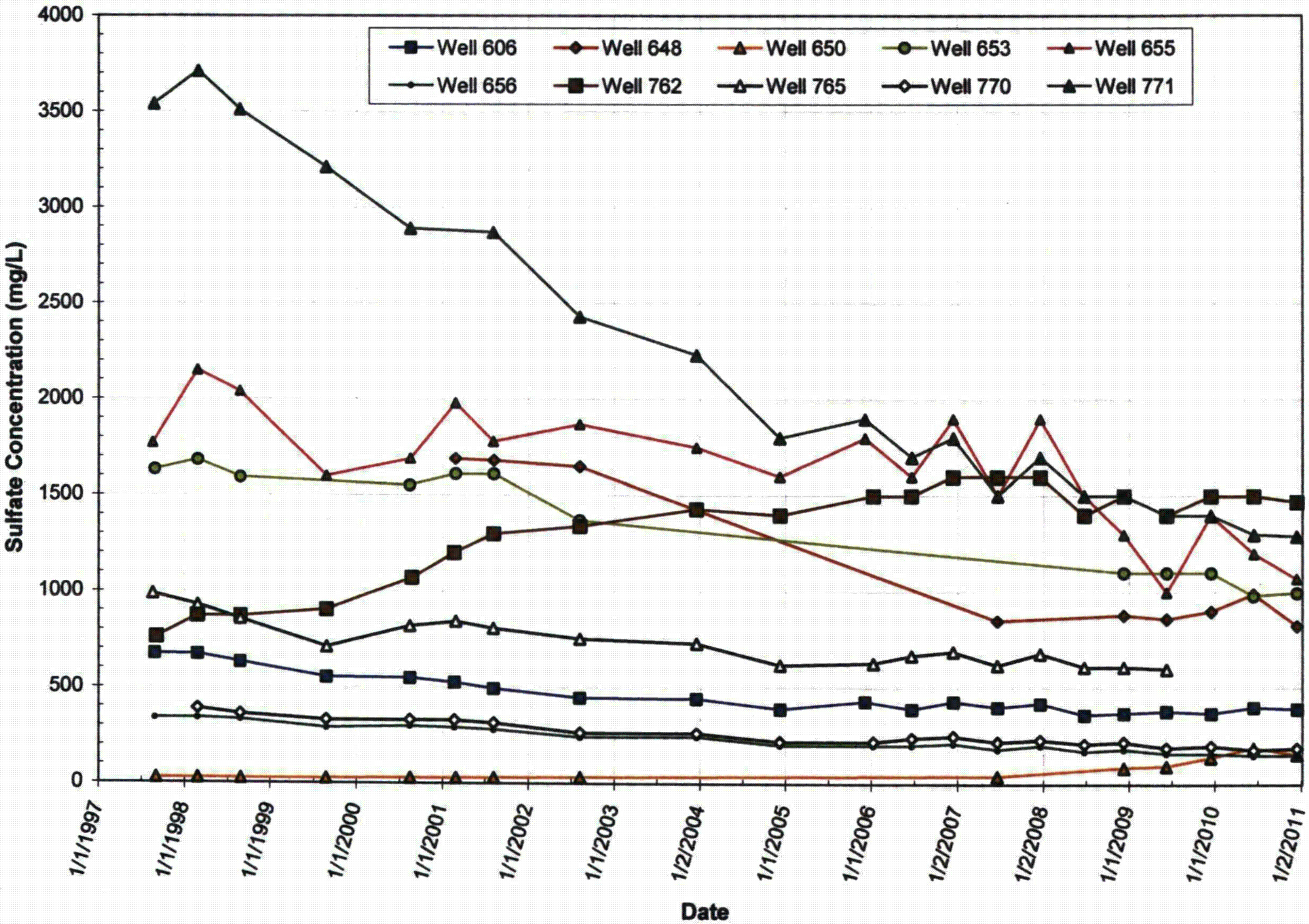

Figure D–14. Sulfate concentrations along and near the plume axis from 1997 to 2010.

In contrast to the mostly declining sulfate levels at the above-mentioned wells, wells 762 and 650 in the northern half of the plume showed clear increases in concentration from 1997 through 2010 (Figures D–10 through D–14). The combination of this latter observation and obviously decreasing concentrations in wells to the south suggests that the center of mass of the sulfate plume had been migrating northward during the 14 years of monitoring. Such an effect comports with the hypothesis that source area phytoremediation has largely, if not completely, cut off site-related influxes of sulfate on the south end of the plume. Alternatively, biologically mediated sulfate reduction is unlikely to have been the cause of such a decrease given that the alluvial aquifer environment is considered to be chemically oxidizing. Regardless of the cause of declining sulfate levels in the southern half of the plume and increasing concentrations in the northern half, the recent occurrence of elevated concentrations at well 650 (156 mg/L in December 2010), some 6,500 ft north of the source area, indicates that sulfate has the potential to migrate farther in the alluvial aquifer than ammonia and nitrate.

The sulfate plumes illustrated in Figures D–10 through D–13 indicate that sulfate contamination at relatively high levels has been observed to the south and southeast of the New Tailings Pile area in addition to the north. Rather than originating as contamination associated with former operations at the Monument Valley site, these latter occurrences of sulfate in groundwater appear to derive naturally from the leaching of gypsum in Moenkopi Formation sandstone and associated gypsiferous soils south and southeast of former tailings areas.

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Appendix E

Active Groundwater Phytoremediation: Native Plant Land Farming

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The Monument Valley pilot studies were designed to provide DOE and Navajo Nation policymakers with an alternative or backup remedy for the alluvial aquifer plume if, over time, natural and enhanced attenuation remedies are found to be inadequate. Native plant land farming is the alternative. At the Monument Valley site, land farming, a type of pump-and-treat remedy, involves irrigating fields of native transplants with nitrate-contaminated groundwater pumped from the alluvial aquifer.

Results show that a land farm with a crop of native fourwing saltbush shrubs should work well as a backup remedy for the plume if other remedies are found to be insufficient. Fourwing saltbush thrived when irrigated with plume water. Plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume remained in the soil profile, perhaps sequestered as gypsum (calcium sulfate); and the land farm produced both forage that is safe for livestock and a native seed crop that could be used by the Navajo Nation for rangeland or mine land reclamation.

LM evaluated land farming as a pump-and-treat option for the Monument Valley nitrate plume. LM considered land farming to be the most feasible active (as opposed to passive) remedy for both nitrate and sulfate in the alluvial aquifer and authorized a pilot study in 2004 (DOE 2004c). If successful as a pilot study, LM may implement land farming if, over time, monitoring shows that natural or enhanced attenuation remedies prove to be inadequate. LM considers land farming to be a form of active phytoremediation.

The land-farm pilot study at Monument Valley involved pumping plume water and irrigating a crop of native shrubs planted on land disturbed during remediation of tailings. With the land-farm option, pumping would continue until nitrate concentrations in the alluvial aquifer drop below the 44 mg/L (or 10 mg/L nitrate as N) MCL.

The land-farm pilot study was designed to serve several functions:

1. Reduce nitrate and ammonia levels in the alluvial aquifer by pumping and irrigating a native shrub crop, converting nitrate and ammonia into useful plant biomass.
2. Reduce sulfate levels in the alluvial aquifer by pumping plume water, irrigating the land farm, and sequestering groundwater sulfate as calcium sulfate in the soil profile, analogous to natural gypsiferous soils in the area.
3. Improve rangeland conditions and produce a cash crop such as native plant seed for use in rangeland revegetation or mine land reclamation.

This section is a summary of (1) a land-farm feasibility study, (2) the pilot study experimental design, (3) results of plant growth, nitrogen uptake, and water management, and (4) results of soil nitrogen and sulfur sampling after 4 years of irrigation with plume water. Appendix H addresses rangeland improvements and other beneficial uses.

E.1 Land Farming Feasibility

The feasibility of irrigating a native shrub crop to recover nitrogen and sulfur from the alluvial groundwater plume rested on several factors:

1. Existing rangeland ecology,
2. Land suitability for irrigation,
3. Adaptability of native plants for cropping,
4. Attainable nitrate levels based on irrigation and pumping rates,
5. Nitrogen uptake rates toxicity to plants,
6. Fate and potential toxicity of soil sulfate, and
7. Crop water requirements and deficit irrigation rates.

These issues were addressed through a series of investigations that included characterization of rangeland conditions and trends, irrigable land classification, discussions of grazing management options with the Navajo Nation, greenhouse studies of crop growth and nitrogen uptake, and an evaluation of potential forage quality, phytotoxicity, and farm soil contamination. Results of these investigations, documented by DOE (DOE 2004b, pp. 8-1 to 8-6), supported a plan to install a field study, in 2005, to evaluate the response of two native shrub crops to different nitrate concentrations in irrigation water.

E.2 Methods

E.2.1 Experimental Design

A factorial field experiment was designed to address several issues that DOE and Navajo Nation would need to resolve before proceeding with a large-scale native plant land farm:

- Which native crop is most efficient in using nitrate?
- What is an optimum irrigation rate to remove as much nitrogen and sulfur as possible while limiting deep percolation and leaching of contaminants back into the aquifer?
- What is the optimum nitrate concentration in irrigation water?
- Will sulfate and nitrate accumulate in the soil and in what forms?
- How productive are the crops?
- Are crops irrigated with plume water safe for livestock? (This issue is addressed in Appendix G.)

A factorial experimental design consists of a treatment structure and a design structure. The treatment structure of an experiment refers to the factors that will be compared and controlled, and design structure refers to how field plots will be arranged and how treatments are assigned to the plots (Milliken and Johnson 1992).

The treatment structure for the land farm pilot study consisted of two main factors: (1) nitrate concentration in irrigation water and (2) crops in the cropping system. Four nitrate treatment levels (as nitrate) were derived from the results of greenhouse studies (DOE 2004b; pp. 8-7 to 8-9): 250 mg/L, a level not likely toxic to crop plants or to livestock feeding on the crop; 500 mg/L, a level not likely toxic to crops but possibly toxic to livestock; 750 mg/L, a level possibly toxic to crops; and a clean water control. Two native shrubs, fourwing saltbush (*Atriplex canescens,* or ATCA) and black greasewood (*Sarcobatus, vermiculatus* or SAVE) were selected as crop plants. Seedlings grown from locally collected seed in a greenhouse were transplanted on a 2 m grid spacing.

A randomized split-block design structsdure developed for the study (Figure E–1) consisted of a 50 × 100 m area divided into four blocks. Four plots in each block received the four different nitrate levels. Each plot was split at random and planted, half with fourwing saltbush and the other half with black greasewood, for a total of 32 equal-size split-plots receiving four replications of 8 different treatment combinations (nitrate level × crop). Figure 1 in the report shows the location of the land farm pilot study as it appeared in 2010.

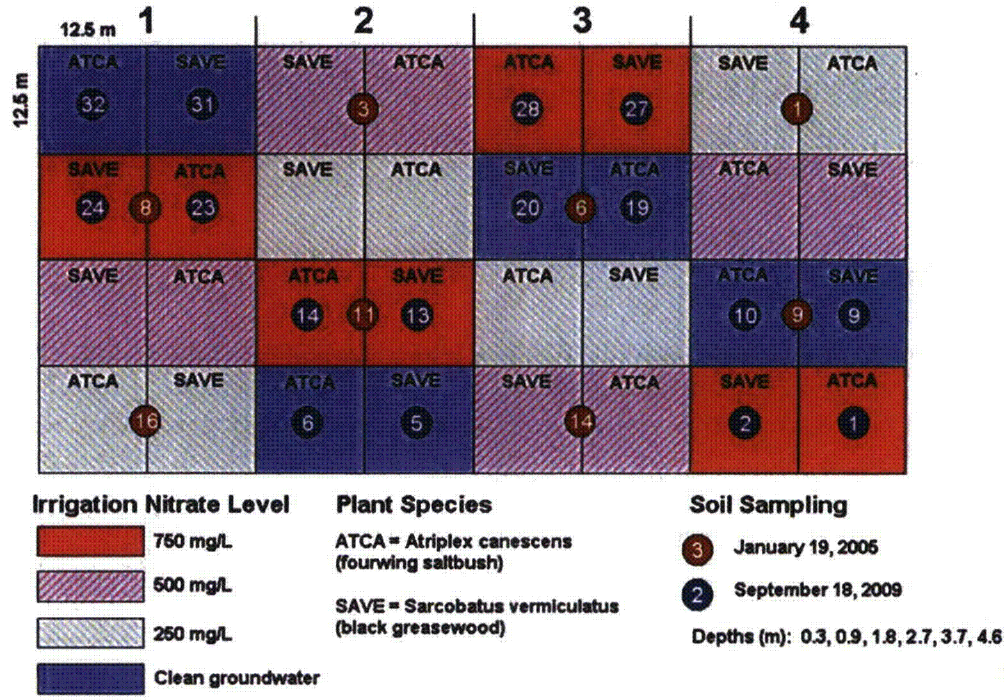

Figure E–1. Illustration of randomized split-block experimental design showing plots for nitrate treatment levels and shrubs species, and soil sampling locations and times.

E.2.2 Irrigation System

Water was delivered to the land farm from two wells: clean water pumped from well 618, a DeChelley aquifer well, and nitrate-contaminated water pumped from well 649, a well completed in 2000 in relatively high-nitrate alluvial groundwater about 283 meters directly north of the land farm. The four nitrate levels were achieved using a drip irrigation system with solenoid valves that alternated between well 618 and well 649. Plants in the control or no nitrate plots received 1 gallon of "clean" water per day from well 618. Plants in the 250 mg/L nitrate plots were irrigated for 30 minutes with water from well 649 and 90 minutes with water from well 618 for a total of 1 gallon per day. Plants in the 500 mg/L nitrate plots were irrigated for 90 minutes with well 649 water and 30 minutes with well 618 water. Plants in the 750 mg/L plots received 1 gallon of contaminated water per day from well 649. Irrigation of the land-farm plots began in fall of 2005

In May 2006, pumping from well 649 was drawing down the groundwater elevation causing the pump to suck air before completing its 2-hour pumping cycle. Hence, the plots assigned the higher nitrate concentrations were receiving less irrigation water than the others. Lowering the pump in the well did not alleviate the problem, nor did splitting the irrigation cycle. As a result, the treatment structure and irrigation schedule were modified to regain consistency in irrigation volumes across all plots. Beginning in May 2007, only plots assigned the 750 ppm nitrate level received plume water from well 649, while all other plots received clean water from well 618.

E.3 Results

E.3.1 Crop Growth, Transpiration, and Nitrogen Uptake

The pilot study results show that during a 4-year monitoring period, fourwing saltbush was superior to black greasewood as a phytoremediation crop. For all treatment combinations, fourwing saltbush had lower mortality rates, grew larger, had greater leaf area and transpiration rates, and took up more nitrogen than black greasewood. Comparisons were made in 2006 and again in 2010 using different methods.

E.3.1.1 2006 Results

In October 2006, survival, growth, and productivity for the different combinations of crops and nitrate irrigation levels were compared. A total of 60 randomly distributed plants (3–5 plants per plot) were measured. Shrub canopy area was estimated from cross-sectional diameters using the formula for an ellipsoid. Plant volume was estimated using the formula for a hemispheroid. Above-ground biomass and total N were estimated based on a canopy volume-weight relationship established previously. Total N was determined by combustion using a CNS-2000 analyzer for 16 individual plants harvested per plot. Plant survival was estimated by census.

In June 2006 we noted that many of the plants had been eaten down by rabbits. Efforts to replace them with new seedlings failed. Black greasewood suffered more from herbivory than fourwing saltbush. Protecting plants in biodegradable mesh cages, in fall 2006, was successful.

Nitrogen uptake was significantly ($P < 0.05$) greater for fourwing saltbush plants harvested from the 750 mg/L nitrate plots compared to plants receiving clean water (DOE 2007; p 3-27). However, estimates of total biomass were not significantly different among treatments, most likely due to variation in irrigation amount and not a response to nitrate toxicity. Plants receiving 750 mg/L nitrate took up no more N than plants receiving 250 mg/L nitrate, reflecting differences in plant growth responses to irrigation.

E.3.1.2 2010 Results

Plant cover and leaf area in the land-farm plots were evaluated in 2010 using a Quickbird satellite image (Figure E–2). The sharp contrast between the bright false-color red fourwing saltbush plots and the adjacent mostly bare black greasewood plots, visible as a checkerboard pattern in Figure E–2, clearly illustrates the greater abundance of fourwing saltbush.

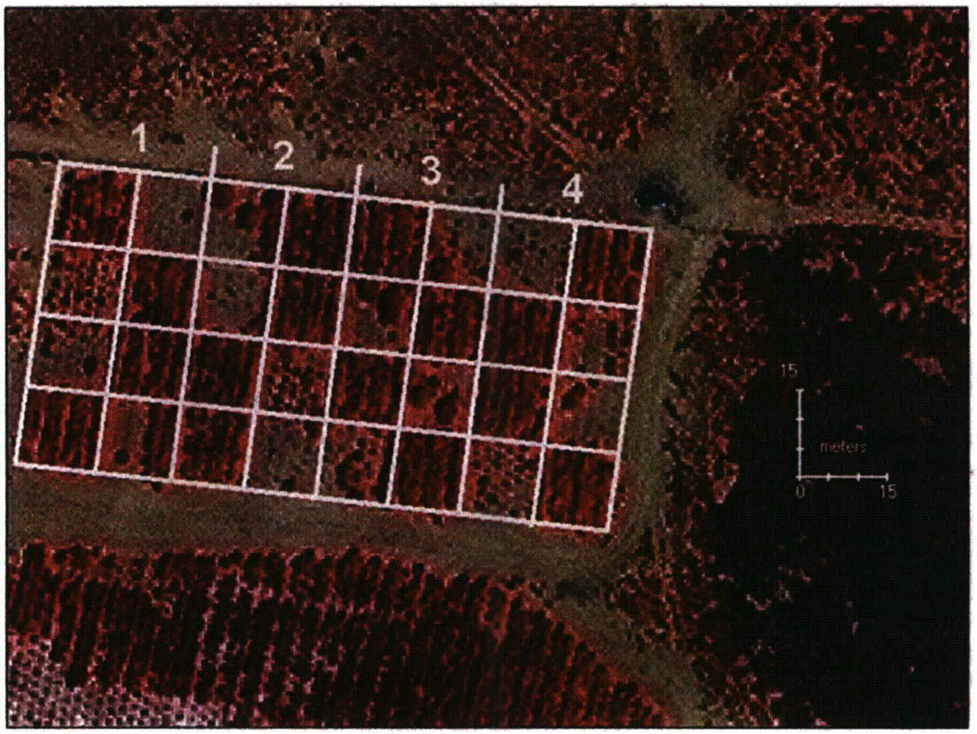

Figure E–2. July 10, 2010, Quickbird image composed of pan-sharpened black-and-white and red-blue-green bands plus the near infrared (NIR) shown in false-color red to highlight plants. Block numbers and plot boundaries, corresponding to Figure E–1, are highlighted in white.

LAI and plant canopy cover were estimated using Quickbird data that was calibrated and validated against ground monitoring data. LAI, defined as green leaf area per unit ground area, is often used to estimate transpiration rate. By 2010, the LAI of fourwing saltbush ($LAI \approx 5.0$) plots was significantly greater ($P < 0.001$) than the black greasewood LAI ($LAI \approx 2.0 - 3.0$) for all nitrate treatments (Figure E–3A). Percent cover, defined as the percentage of ground surface area beneath or "covered" by plant canopy, was more variable but also significantly greater ($P < 0.001$) in fourwing saltbush plots (Figure E–3B).

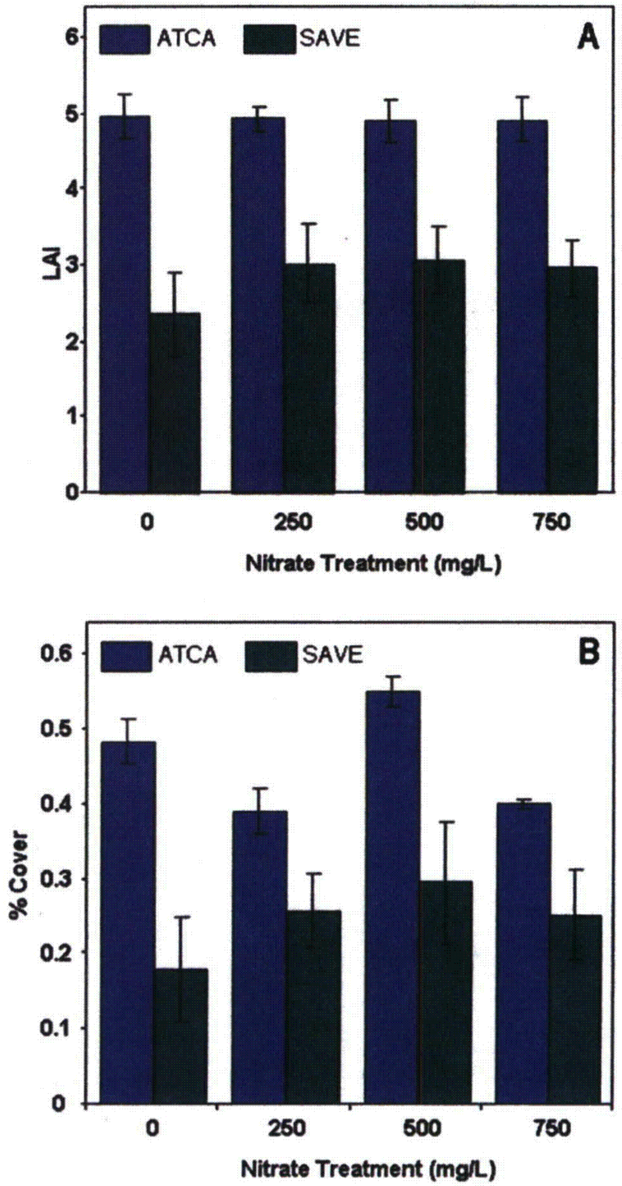

*Figure E–3. (A) Leaf area index (LAI) and (B) percent cover of fourwing saltbush (*Atriplex canescens*, or ATCA) and black greasewood (*Sarcobatus vermiculatus*, or SAVE) for irrigation water nitrate treatments. Bars are one standard error of the mean. Analysis of variance (ANOVA) results show that species differences are significant at $P < 0.001$.*

Field observations revealed that much of the LAI and percent cover in the black greasewood plots, estimated using Quickbird, is attributable to volunteer fourwing saltbush plants. The Quickbird analysis did not differentiate the two species. Therefore, differences in the LAI and percent cover of the two species were likely greater than the Quickbird interpretation indicates.

Estimates of LAI and percent plant cover were derived from a July 2010 Quickbird satellite image with 0.5 m resolution in the visible spectrum and 2 m resolution for the NDVI. NDVI is calculated from red and NIR bands. Percent cover was estimated by classifying pixels as either bare soil or vegetation using a program in ERDAS software (www.erdas.com). Estimates using this approach were compared to cover estimated from a visual inspection of images using a point intercept method (Figure E–4).

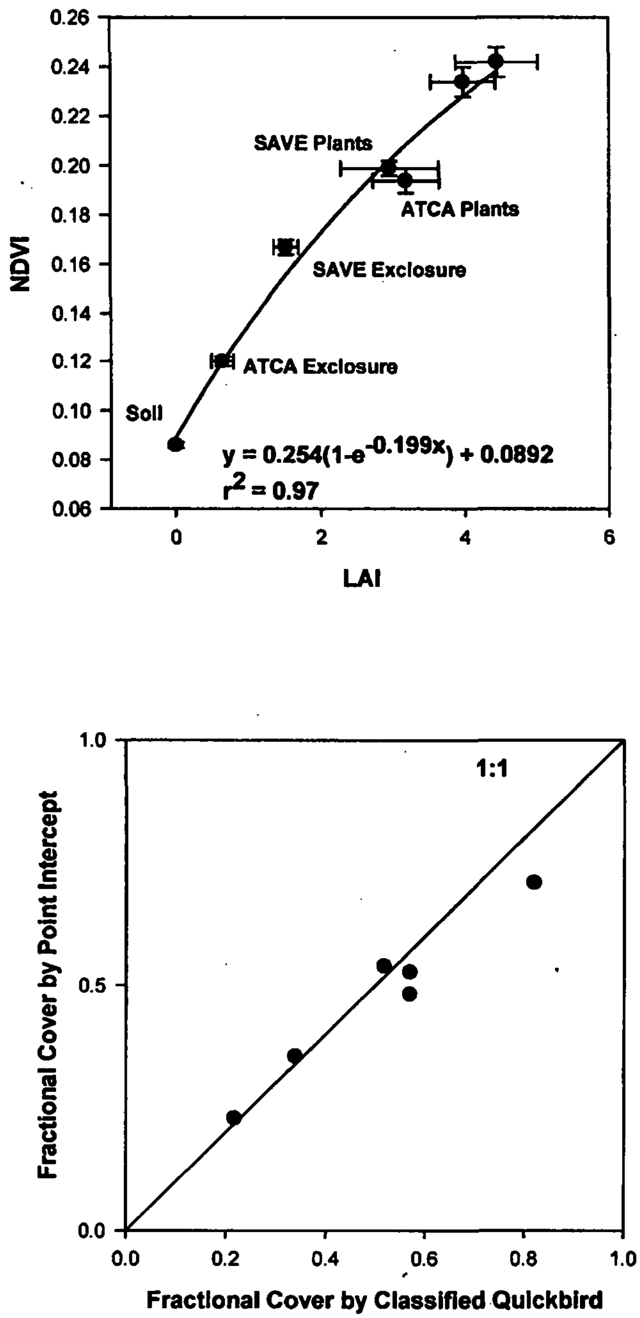

Figure E–4. Top: LAI measured on the ground by leaf harvesting versus NDVI using Quickbird. Bottom: Fractional cover estimated visually on Quickbird using a point intercept method versus an automated method using a pixel classification program in ERDAS.

LAI was calculated from NDVI in areas of interest using a regression of LAI values measured in 2007 with a Licor 2000 LAI Meter against leaf harvesting data. LAI was measured on individual plants and extended to stands of plants by multiplying LAI by fractional cover determined on the July 2010 Quickbird image (Figure E–4).

Although survival and growth of fourwing saltbush far exceeded black greasewood during the 5-year study, greasewood may take longer to establish and so, over a longer period of time, may close the gap with fourwing saltbush. By 2010, the few 11-year old greasewood seedlings planted in 1999 in the source area (Appendix B) were about the same size as their fourwing saltbush neighbors.

E.3.2 Soil Water Monitoring

Volumetric soil water content (θ) was monitored monthly during the growing season from March 2006 through October 2010 using a neutron hydroprobe (Gardner 1986). Thin-walled polyvinyl chloride access tubes, 457 cm deep by 5.7 cm i.d., were installed in 16 locations in 2002 during construction of an earlier land-farm study (DOE 2002). DOE terminated the earlier study before the installation was complete. In the current experimental design, eight access tubes occur within ATCA plots and the other eight within SAVE plots. Neutron counts were recorded at depths of 30, 61, 91, 122, 152, 183, 213, 244, 274, 305, 335, 366, 396, 427, and 457 cm.

The neutron hydroprobe was calibrated in barrels using soils from Monument Valley, compacted to achieve the bulk density of the land-farm soil, and wetted incrementally to prescribed gravimetric water contents. The calibration produced the following linear relationship:

$$\theta = 1.93 \times 10^{-5} * (\text{neutron count} - 1.81 \times 10^{-2})$$

Soil water storage (S) was calculated from neutron hydroprobe measurements of θ using a trapezoidal approximation by Green et al. (1986) as follows:

$$S = \theta_1 Z_1 + \sum_{i=2}^{n} [(\frac{\theta_{i-1} + \theta_i}{2})(Z_i - Z_{i-1})]$$

where:

θ_1 and Z_1 are the water content and depth for the uppermost measurement

θ_i is the volumetric water content measured at the *i*th point in the profile

Z_i is the depth of the *i*th point in the profile

n is the total number of points.

Soil profiles were significantly drier in ATCA plots than in SAVE plots, reflecting the higher survival, productivity, and transpiration of ATCA as a land-farm crop. Mean values of θ for ATCA (0.11) and SAVE (0.14), averaged over all plots, depths, and months, were significantly different at $P < 0.001$. Mean values of S for ATCA (691 mm) and SAVE (929 mm) were also significantly different at $P < 0.001$.

Time series of soil water storage (S) over the 4-year monitoring period reflect contrasts in the growth and development of ATCA and SAVE crops (Figure E–5). The SAVE plots started out slightly wetter than ATCA plots. However, after irrigation commenced, S values increased steadily over the first two years for both species. But in 2008, the third growing season, the ATCA plots began to dry while the SAVE plots continued to get wetter. This is likely attributable to an increase in leaf area and transpiration by ATCA as illustrated in Figure E–2.

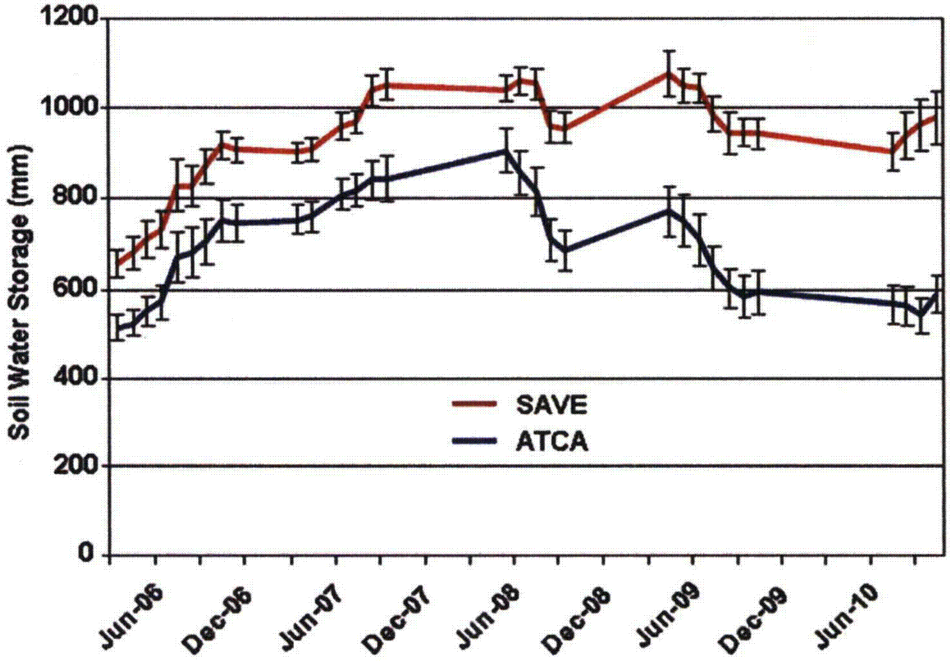

Figure E–5. Changes in soil water storage in Sarcobatus vermiculatus *(SAVE) and* Atriplex canescens *(ATCA) land-farm plots monitored monthly during the growing season using a neutron hydroprobe. Error bars = standard error of the mean.*

By 2010, ATCA that had volunteered in the SAVE plots were maturing and leaf area (Figure E–3) and transpiration rates were likely high enough to cause the slight drop in water storage (Figure E–5).

E.3.3 Soil Nitrogen and Sulfur

Land-farm soil sampling data show that irrigation with plume water resulted in little if any accumulation of soil nitrate, probably due in part to plant uptake and denitrification in the fourwing saltbush plots, and in part to leaching in plots where transpiration was inadequate. However, irrigation with plume water did result in an accumulation of sulfate in the soil profile, and perhaps sequestration as calcium sulfate (gypsum).

Soil profiles in the land farm were sampled in 2005, at the beginning of the study, and again in 2009 (Figure E–1). The objective of the 2005 sampling, which occurred before the design layout was finalized, was to develop mean baseline levels of nitrate, ammonia, and sulfate and to map spatial distributions in the land farm. Soil profiles were sampled at eight locations. The objectives in 2009 were (1) to determine changes in mean soil levels of nitrate, ammonia, and sulfate over time and (2) to test for treatment effects. In 2009, soil profiles were sampled in the center of all plots receiving clean water and 750 mg/L nitrate water. During both sampling events and at all sampling locations, samples (approximately 500 g each) were removed from the soil profile at depths of 1, 3, 6, 9, 12, and 15 ft using a 2-inch diameter hand auger.

Figure E–6 and Figure E–7 map soil nitrate and sulfate distribution in the land farm in 2005. The maps, created using EVS software, are mean concentrations of nitrate and sulfate for all depths at each sampling location. Results show that baseline concentrations of both nitrate and sulfate varied considerably across the site, ranging from < 5.6 µg/g (detection limit) to 778 µg/g for nitrate as nitrogen, and from < 25 µg/g (detection limit) to 4,185 µg/g for sulfate. The high spatial variability in soil nitrate and sulfate in 2005 may have masked detection of some treatment effects when soil profiles were sampled again in 2009.

Figure E–8 compares 2005 with 2009 mean values of soil nitrate, ammonia, and sulfate for all treatments combined. Values are means for all depths and locations. Analysis of variance (ANOVA) results show that mean ammonia-N and nitrate-N values changed little over four years of irrigation, but sulfate levels were significantly less by 2009 ($P < 0.001$), possibly due to leaching in the black greasewood plots. An ANOVA evaluation of treatment effects in 2009 indicated that soil sulfate levels were significantly greater ($P < 0.001$) in plume water plots than in clean water plots, suggesting an accumulation of sulfate from irrigation with plume water. Results also show that mean nitrate-N levels are significantly different for water and plant treatments at $P < 0.1$. Figure E–9 values are means of all depths for each treatment.

The source of treatment effects on soil nitrate-N depicted in Figure E–9 was clarified by comparing profiles of nitrate concentrations with depth (Figure E–10). ANOVA results show that nitrate-N levels in the lower soil profile of the ATCA (fourwing saltbush) plots were significantly greater than all other upper or lower profiles ($P < 0.001$). One interpretation of the nitrate profiles, and the overall loss of sulfate between 2005 and 2009, is that the poor growth and low transpiration in SAVE (black greasewood) plots allowed leaching of nitrate and sulfate whereas high productivity and transpiration in ATCA (fourwing saltbush) plots limited leaching and caused nitrate accumulation in the lower profile.

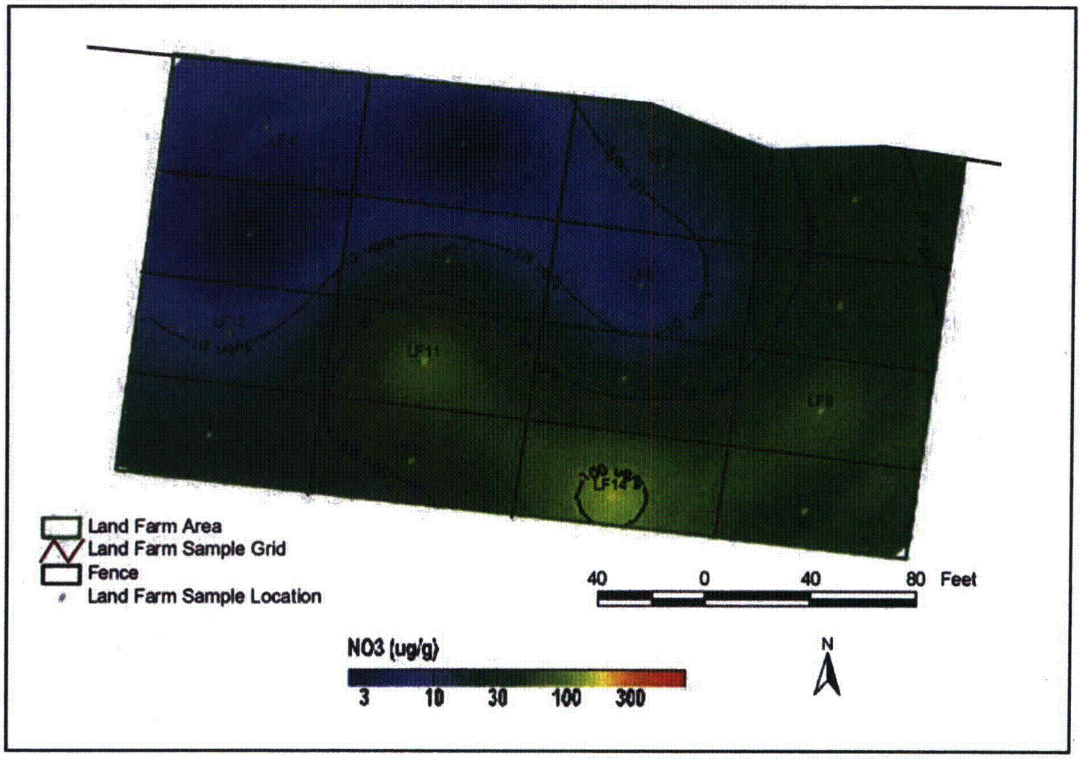

Figure E–6. Map of baseline soil nitrate distribution in the land farm created using mean concentrations at each sampling location.

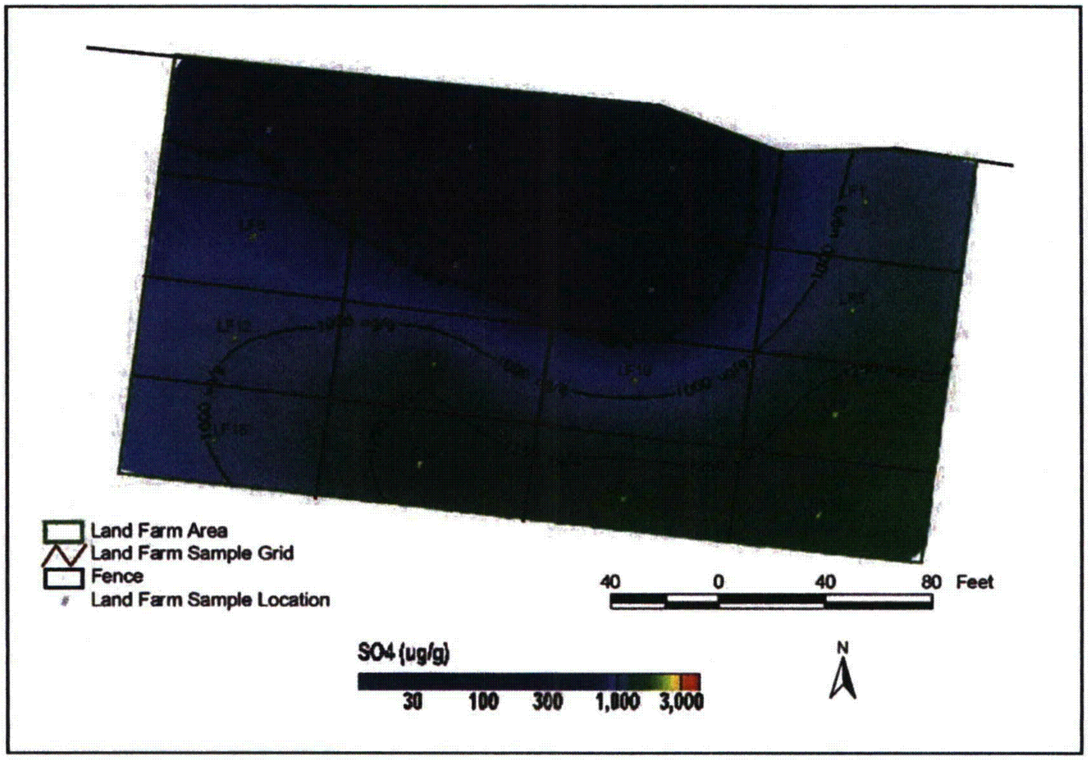

Figure E–7. Map of baseline soil sulfate distribution in the land farm created using mean concentrations at each sampling location.

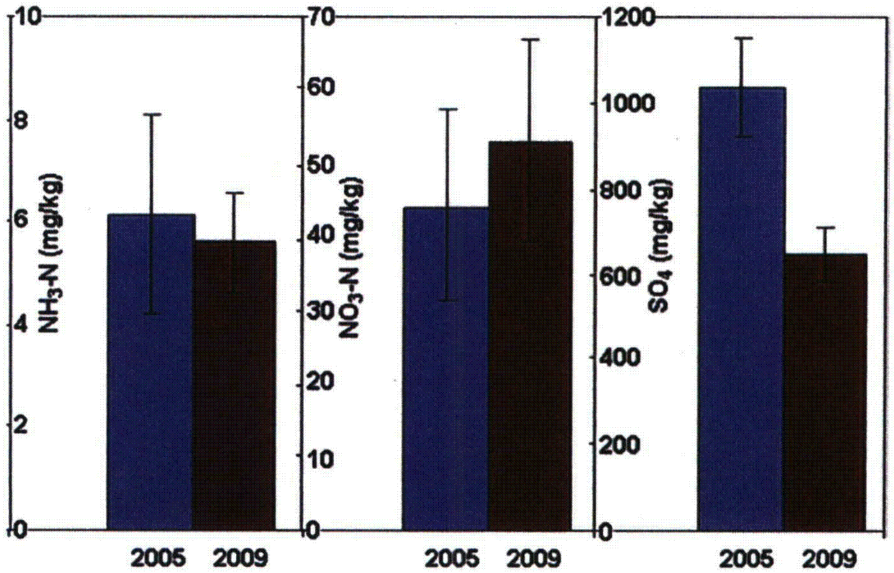

Figure E–8. Comparison of mean soil ammonia-N, nitrate-N, and sulfate concentrations for combined treatments in the land farm study in 2005 and 2009.

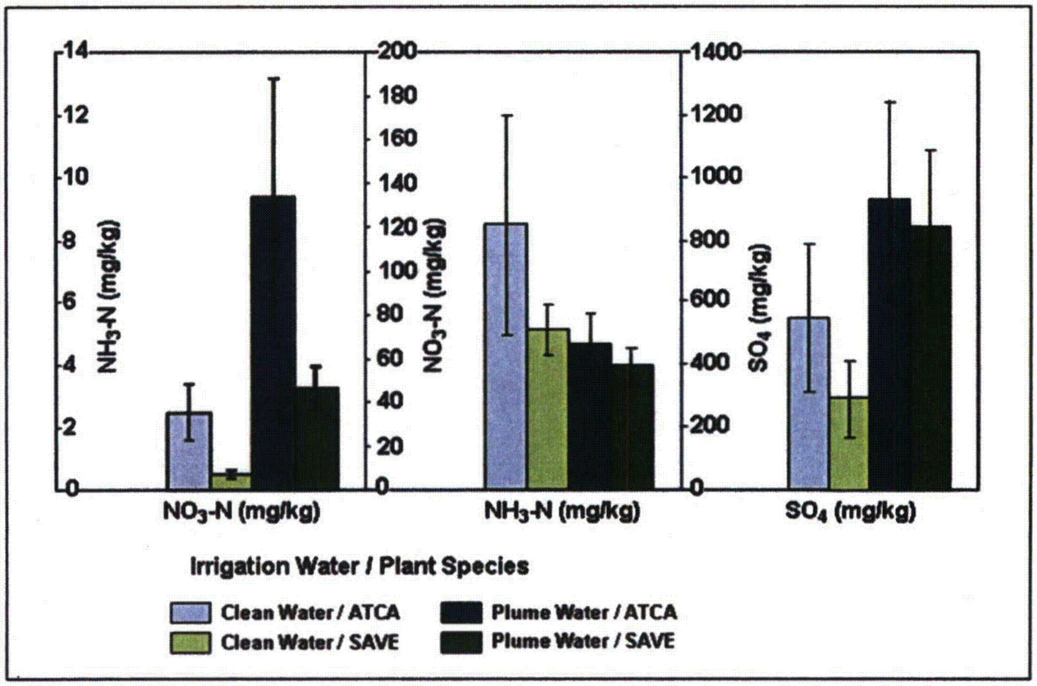

Figure E–9. Comparisons of soil ammonia-N, nitrate-N and sulfate levels in 2009 for the different irrigation water and plant treatments in the land farm study.

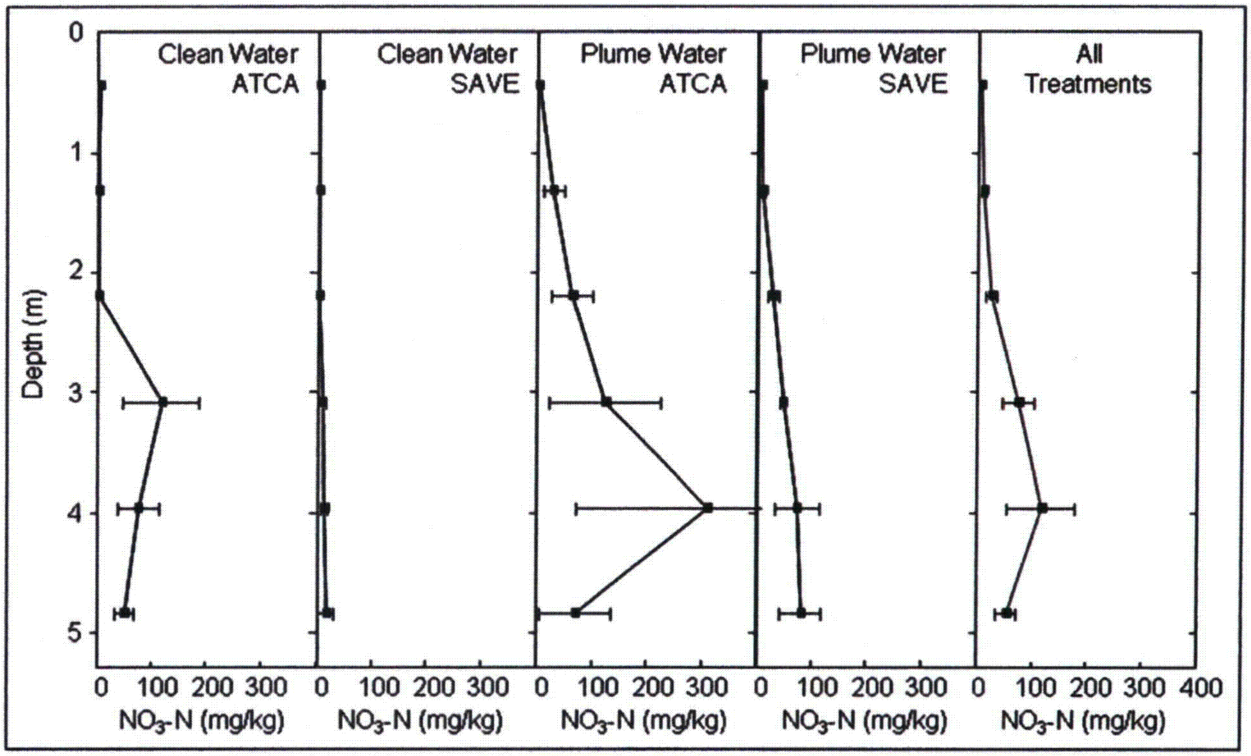

Figure E–10. Mean soil nitrate-N with depth for irrigation water and plant treatments in the Monument Valley land farm study.

Appendix F

Remote Sensing Monitoring of Phytoremediation

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A remote sensing protocol was developed as an efficient means for long-term monitoring of vegetation and ET. If phytoremediation becomes part of the final remedy for the source area or the plume, phreatophyte health and transpiration would be key long-term indicators of remedy performance. Development of the remote sensing protocol involved calibration of satellite images with important characteristics of vegetation as measured on the ground. Satellite images included annual Quickbird and Landsat images, and 16-day images from the Moderate Resolution Imaging Spectrometer (MODIS) sensors on the Terra satellite. The key vegetation performance indicators are leaf area index, fractional vegetation cover, and plant water use (ET).

The successful calibration allowed project scientists to quantify and compare—on a landscape scale—effects of grazing and revegetation practices on phreatophyte health and phytoremediation performance. Prior to the pilot studies, much of the Monument Valley site landscape had been heavily grazed, leaving populations of native phreatophytes (fourwing saltbush and black greasewood) in poor ecological condition. Over the past 10 years, however, livestock numbers and grazing pressure has been reduced over the site, and, using the remote sensing protocol, project scientists have quantified improvements in the health, fractional cover, and ET of phreatophyte populations. Results show that, as a consequence of improved grazing practices, the plume area appears to have converted from an area of recharge (less water used by plants than arrives as precipitation) to one of discharge (plant water use exceeds precipitation), indicating that water from the plume is being removed. This is good news with respect to phytoremediation. A healthy plant community may be capable of slowing or stopping the further migration of the contaminant plume.

The Monument Valley site covers about 230 ha, including the source area and the surface footprint over the contamination plume in the alluvial aquifer. Vegetation can play a key role in controlling the water balance of a desert site such as Monument Valley (Naumber et al. 2005; Nichols 1993, 1994, 2000). The two dominant shrubs at the site are *Sarcobatus vermiculatus* (SAVE) and *Atriplex canescens* (ATCA), both of which are phreatophytes that extract water from the vadose zone as well as the alluvial aquifer (Jordan et al. 2008). When these shrubs are protected from grazing they can develop abundant plant cover (McKeon et al. 2006) with high transpiration rates (Glenn et al. 2009). As phreatophytes, populations of these species, when healthy, can transpire more water than arrives as precipitation, with the difference extracted from groundwater. Theoretically, this groundwater discharge will slow or reverse the spread of groundwater contamination away from the source area. Then again, this site has a history of heavy grazing by livestock, which can greatly reduce plant health and transpiration rates, potentially accelerating the spread of contaminants away from the source area due to recharge of the aquifer from percolation of precipitation over the site and runoff from adjacent uplands.

Contaminants in the source area soils and in the alluvial aquifer include nitrate, ammonium, and sulfate. Concentrations of all three appear to be gradually decreasing due to natural attenuation processes as characterized by monitoring and modeling (Appendix D). However, natural or even enhanced attenuation of the source area and plume will likely take several decades (Appendix C). A healthy plant community may reduce the risk that contaminants will migrate further away from the site during this time. Therefore, monitoring the progress of natural and enhanced attenuation should include tracking the health or condition of phreatophyte populations in response to changing land management practices.

Remote sensing can provide economical, long-term, non-intrusive monitoring of phreatophyte health and water use. This section is an overview of the methods project scientists used to develop a monitoring protocol. The methods essentially are a calibration of fractional vegetative cover, LAI, and ET as measured extensively on the ground at the site from 1999 to 2010, and as measured by satellite imagery. More complete documentation of the methods development is appended as a technical journal manuscript. In addition to describing methods development, this section also gives an overview of the application of the protocol to document changes from 2000 to 2010 in phreatophyte cover, ET, and the site water balance in response to changing grazing management practices and the maturation of phytoremediation plantings.

F.1 Land Areas Monitored

Pilot remediation studies at the site are documented in DOE Status Reports (Appendix I). Figure F–1 and Figure F–2 show different natural and planted vegetation units that were of importance for the pilot studies. In 1999, a 1.7 ha plot, designated the Old Field, was established in the fenced source area that included the former New Tailings Pile and evaporation ponds. This area was planted primarily with fourwing saltbush shrubs with about 1 percent black greasewood shrubs, on a 2 m × 2 m spacing. These plantings have been drip-irrigated each growing season since 1999, from April to October, with between 0.16 to 0.36 m yr^{-1} of non-contaminated water. This Old Field was established over hot spots of soil nitrate and ammonium contamination. Additional areas to the north, south, and west of the plot, and over the former evaporation ponds, were planted in 2006 based on additional contaminant surveys (Appendix B). In Figure F–2 these areas are designated New Fields North, West, South and Evaporation Pond (EP), respectively, for a total area of 1.6 ha. These plantings have been drip-irrigated since 2006 similar to the Old Field.

Four small grazing exclosure plots (50 m × 50 m fenced areas) were also established to determine vegetation response to grazing exclusion (Appendix C, Section C.1.3). Two of these, designated ATCA Exclosure and SAVE Exclosure, were established in 2005 around existing plant communities overlying the alluvial aquifer plume. Two more plots, designated East Exclosure and West Exclosure, were established in 2006 in an area that had been denuded. These plots were also planted primarily with fourwing saltbush shrubs on a 2 m × 2 m spacing and drip irrigated similar to the other plantings. In addition, an irrigated area designated Pilot Farm (50 m × 100 m) containing small plots of fourwing saltbush and black greasewood was established to evaluate whether irrigating fields of native transplants with nitrate-contaminated water pumped from the alluvial aquifer could be used as an alternative groundwater remedy.

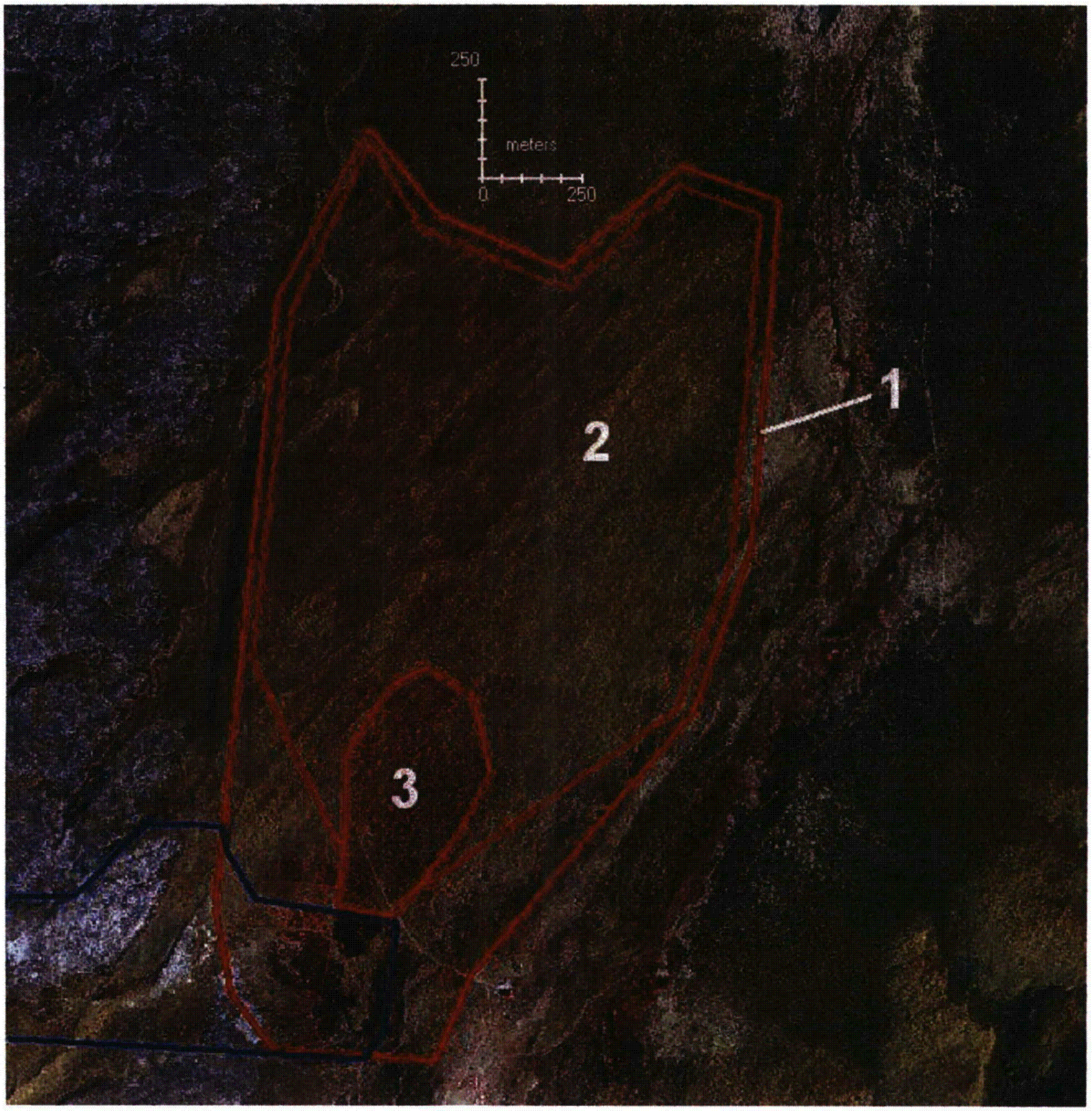


Figure F–1. Areas of interest at the Monument Valley site: (1) the whole site; (2) the Outside ATCA zone; and (3) the Outside SAVE zone. The blue line shows the fence line around the source area.

Figure F–2. Areas of interest at the Monument Valley UMTRA site: (4) the Old Field; the New North (5), New South (6), New West (7), and Evaporation Pond Fields (8); irrigated and planted West (9) and East (10) livestock exclosures; unirrigated exclosures in natural stands of ATCA (11) and SAVE (12); the pilot land farm (13); and a volunteer stand of ATCA (14) inside the source area fence.

Additional areas of interest in Figure F–1 and Figure F–2 are a stand of volunteer fourwing saltbush plants that established inside the site fence and immediately adjacent, a natural stand of dense, mainly black greasewood plants north of the fence, designated Outside SAVE. Sparse stands of mainly fourwing saltbush plants, designated Outside ATCA, dominated the area overlying the plume to the north.

F.2 Ground Vegetation Surveys

Annual surveys of plant cover, LAI, and standing biomass were conducted from 2000 to 2010 within the areas shown in Figure F–1 and Figure F–2. In 2006 and 2007, transpiration of individual fourwing saltbush and black greasewood plants were measured, using sap flux sensors, in the ATCA and SAVE Exclosure plots and on adjacent grazed plants (Glenn et al. 2009). Although sap flux sensors measure just the transpiration component of ET, the site soil is normally dry and direct evaporation from the soil is assumed to be fairly low, so, by convention, the term ET is used in this report for water loss through the plants. Livestock stocking rates were not directly monitored during this period, but from 2000 to about 2004, grazing pressure was significant, as indicated by poor plant health. After the green-up of shrubs in May and June each year, sheep, cattle, and horses grazed the new growth of both species, removing most of the new leaves and even pruning back new and old shoots. Starting in 2005, grazing pressure appeared much lower. In addition, the source area has been fenced since 1999, excluding grazing except occasionally when fences are down and animals enter.

F.3 Remote Sensing Methods

Time-series imagery from 2000 to 2010 was obtained from the MODIS sensors on the Terra satellite (250 m resolution). This satellite has nearly daily coverage of the globe and data are supplied as preprocessed vegetation indices or other products in 16-day composite increments. Project scientists used the MOD13Q1 Enhanced Vegetation Index (EVI) product for analyses of ET. EVI data were combined with maximum daily temperature data (obtained from the PRISM website) to calculate ET using an algorithm calibrated with sap flux data collected onsite (Glenn et al. 2009). Visual changes in site vegetation were also analyzed using Landsat TM-5 images obtained in the summers of 2000, 2005, 2007, and 2009.

Fine-level estimates of percent cover and LAI were made on Quickbird satellite images obtained for the summers of 2006, 2007, 2009, and 2010, with 0.5 m resolution in visible and 2 m resolution for the NDVI, calculated from red and NIR bands. Percent cover was estimated by converting pixels into two classes, representing bare soil or vegetation, using an unsupervised classification program in ERDAS software. The accuracy of the classification system was tested by comparing these estimates of groundcover with estimates determined by visual inspection of images using a point intercept method. This was accomplished for areas representing a wide range of cover conditions by placing a grid over the area of interest on the Quickbird image and scoring each grid intersection as either vegetated or bare soil in Adobe Photoshop. The same areas were then classified in ERDAS to determine percent cover by the automated method.

LAI was calculated from NDVI in areas of interest using a regression of measured LAI values from a Licor 2000 LAI Meter in 2010 and leaf harvesting methods in 2007. LAI was measured on individual plants and was extended to stands of plants by multiplying LAI by fractional cover determined on a Quickbird image acquired on July 10, 2010.

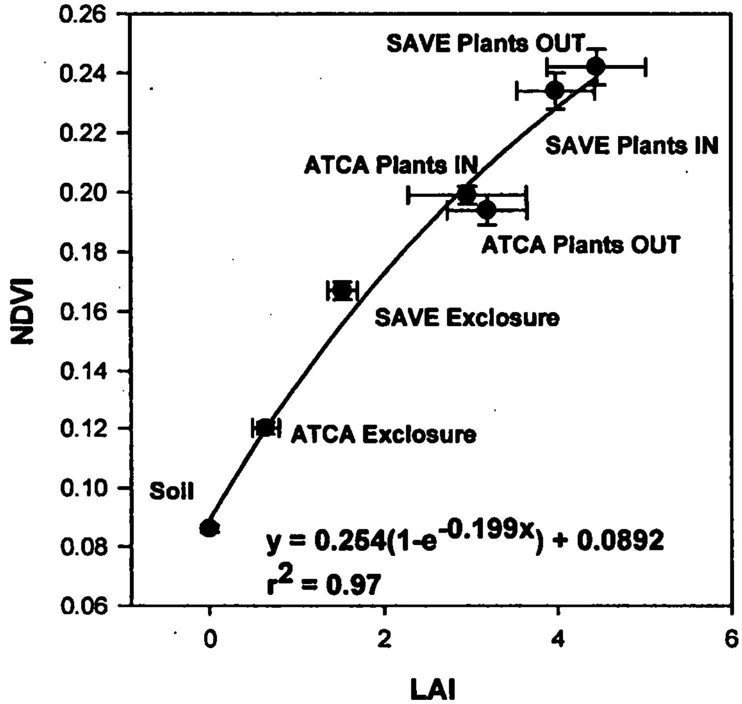
F.4 Vegetation Monitoring Results

F.4.1 Site Conditions in 2010 by Quickbird

Ground measurements of LAI determined by leaf-harvesting methods were accurately predicted by NDVI values (Figure F–3A). Fractional cover determined on a two-class Quickbird image had a near 1:1 correspondence with percent cover determined by ground transect methods (Figure F–3B). Table F– 1 gives NDVI, percent cover, and LAI values for areas of interest in Figure F–1 and Figure F–2. The Old Field and Inside ATCA areas had high cover but low LAI. Both of these stands had grown to exceed their water supply and were undoubtedly water stressed. They were also composed of older plants that had accumulated a great deal of thatch and woody stem material within the stands. The most vigorous planted area was the New Field North, with 60.1 percent cover and an LAI of 1.65. The other New Field areas had lower cover and LAI, especially the New Field West, perhaps due to chemical contaminants in the soil that also affected portions of the Old Field. The irrigated plants in the East and West Exclosures and the Pilot Farm also had high cover and LAI. The unirrigated ATCA and SAVE Exclosures each had higher cover and LAI than unprotected plants in Outside SAVE and Outside ATCA zones, showing that protection from grazing enhances plant growth. Over the whole site, plant cover averaged 31.2 percent and LAI was 0.65. Fourwing saltbush and black greasewood accounted for about half of the total vegetation cover as determined by ground transect methods.

Table F– 1. NDVI, percent vegetation cover, and leaf area index for areas of interest at the Monument Valley site based on analysis of a July 10, 2010, Quickbird satellite image.

Site No.	Description	NDVI	Cover (%)	LAI
1	Whole Site	0.172	31.2	0.65
2	Outside ATCA	0.175	29.0	0.70
3	Outside SAVE	0.193	40.9	0.97
4	Old Field	0.143	51.4	0.69
5	New Field North	0.230	60.1	1.65
6	New Field South	0.167	31.1	0.58
7	New Field West	0.120	4.1	0.16
8	New Field EP	0.141	27.8	0.18
9	Exclosure West	0.200	76.3	1.08
10	Exclosure East	0.223	48.0	1.44
11	ATCA Exclosure	0.195	35.3	1.01
12	SAVE Exclosure	0.203	66.9	1.13
13	Pilot Farm	0.208	31.4	1.20
14	Inside ATCA	0.147	70.8	-



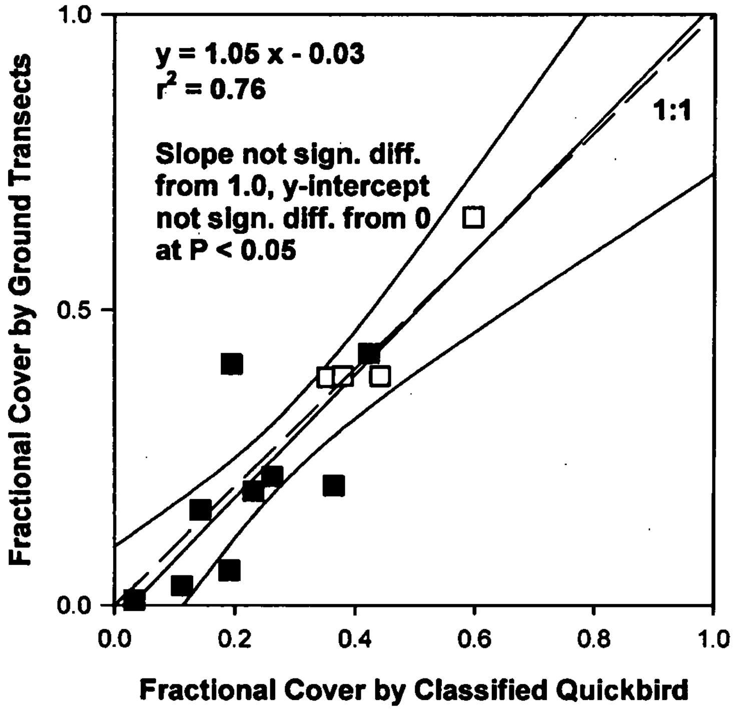


Figure F–3. (Above) Relationship between leaf area index (LAI) measured by leaf-harvesting and fractional ground cover measurements inside and outside exclosure plots and NDVI values on 2007 and 2010 Quickbird images. (Below) Relationship between fractional cover measured inside and outside exclosure plots by line transects and fractional cover estimated on classified Quickbird images. Closed squares are from 2007 measurements and open squares are from 2010.

F.4.2 ET and Vegetation Changes, 2000–2010 by MODIS and Landsat

Landsat images show a clear increase in vegetation intensity over the site from 2000 to 2009 (Figure F–4). Estimated ET rates by MODIS imagery of the site over four years are in Figure F–4. The area inside the fence showed a marked increase in ET after 2005 due to the growth of the irrigated and volunteer plants. However, the Outside ATCA and Outside SAVE areas also showed an increase in ET after 2005. This was attributed to reduced grazing compared to earlier years. ET measured by sap flow sensors in 2006 and 2007 matched the rates predicted from MODIS EVI and the maximum daily temperature. Figure F–5 shows no clear relationship between ET and precipitation on a monthly basis over the study period. This was also evident from a plot of mean monthly values of ET and precipitation averaged over multiple areas and years (Figure F–6). ET followed a regular seasonal pattern, low in winter and high in summer, whereas precipitation was highest in late summer and winter, and was lowest in early and mid-summer when ET was highest. This is a typical pattern for desert phreatophytes in the western U.S. (Lin et al. 1996).

Annual totals of potential ET (ET_0), estimated ET for areas of interest at the site, and precipitation are in Table F–2. ET for Inside, Outside SAVE, and the Whole Site areas were significantly ($P < 0.05$) correlated with the year; the correlation for the Outside ATCA area was marginally significant ($P = 0.078$). The correlations with the year were due to the increase in ET across the site after 2004 (see Table F–2). This increase was due presumably to reduced grazing, since neither ET_0 or precipitation increased over that time period. ET was not significantly correlated with precipitation. However, onsite measurements of precipitation were only available from 2007 to 2010; data for previous years were interpolated from widely spaced reporting stations by the PRISM Climate Group (University of Oregon) and they did not match well with the onsite data for the years of overlap. For the 4 years for which onsite precipitation data were available, both precipitation and ET were lowest in 2009 and highest in 2010, suggesting that precipitation is one of the factors controlling annual ET.

Figure F–5 and Table F–2 show that fourwing saltbush and black greasewood plants are able to utilize a large portion of the annual precipitation even when it arrives at a time when plants are not active; presumably winter rains percolate into deep soil layers and are used to support plant ET in summer (Lin et al. 1996). High rainfall use efficiency is evident by comparing annual precipitation with annual ET. Over the whole site, ET was equal to 99 percent of precipitation from 2005 to 2010, compared to only 78 percent from 2000 to 2004.

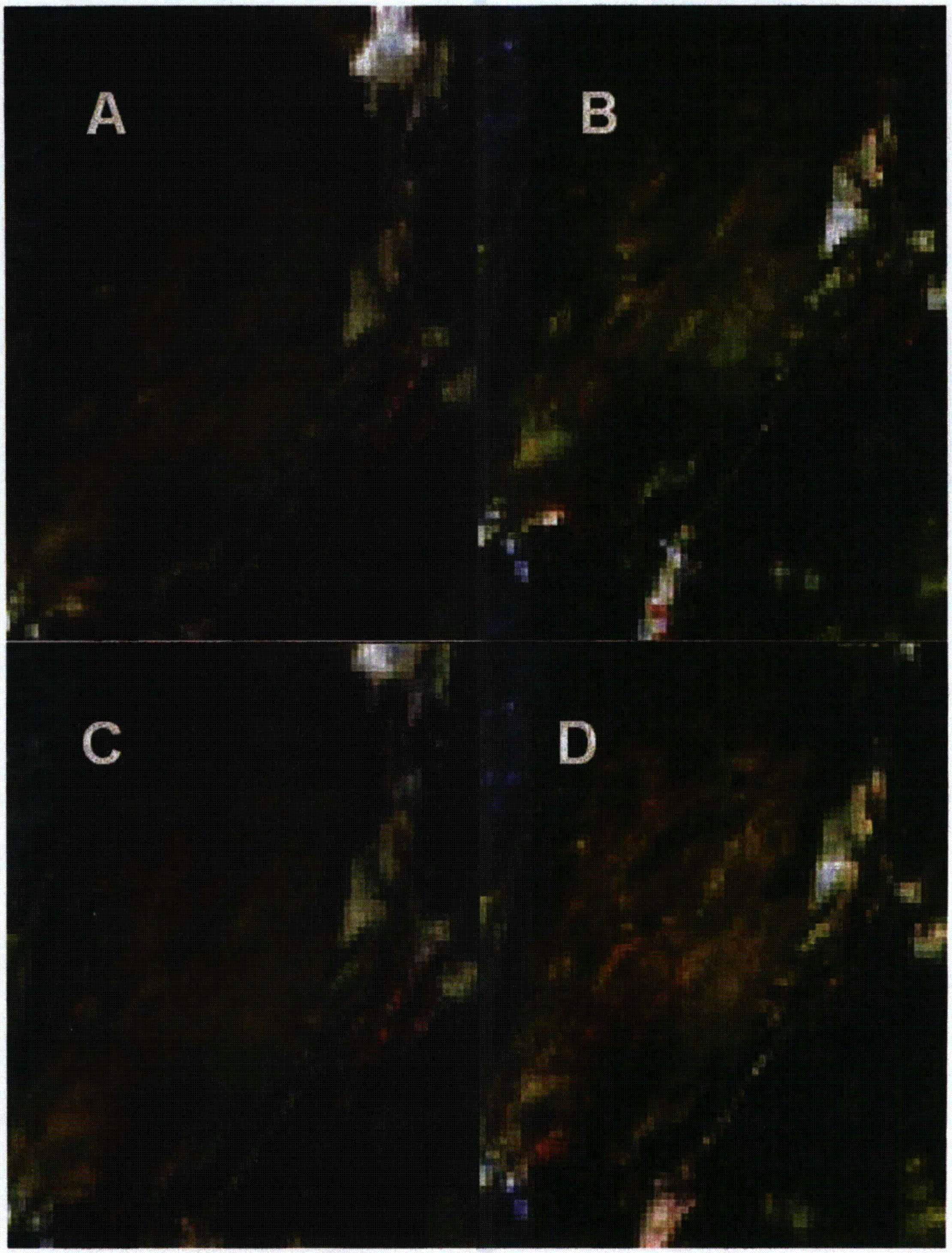


Figure F–4. False-color Landsat Thematic Mapper 5 images of the Monument Valley site with the near infrared band denoting vegetation shown in red. Images are summer scenes for 2000 (A), 2005 (B), 2007 (C), and 2009 (D).

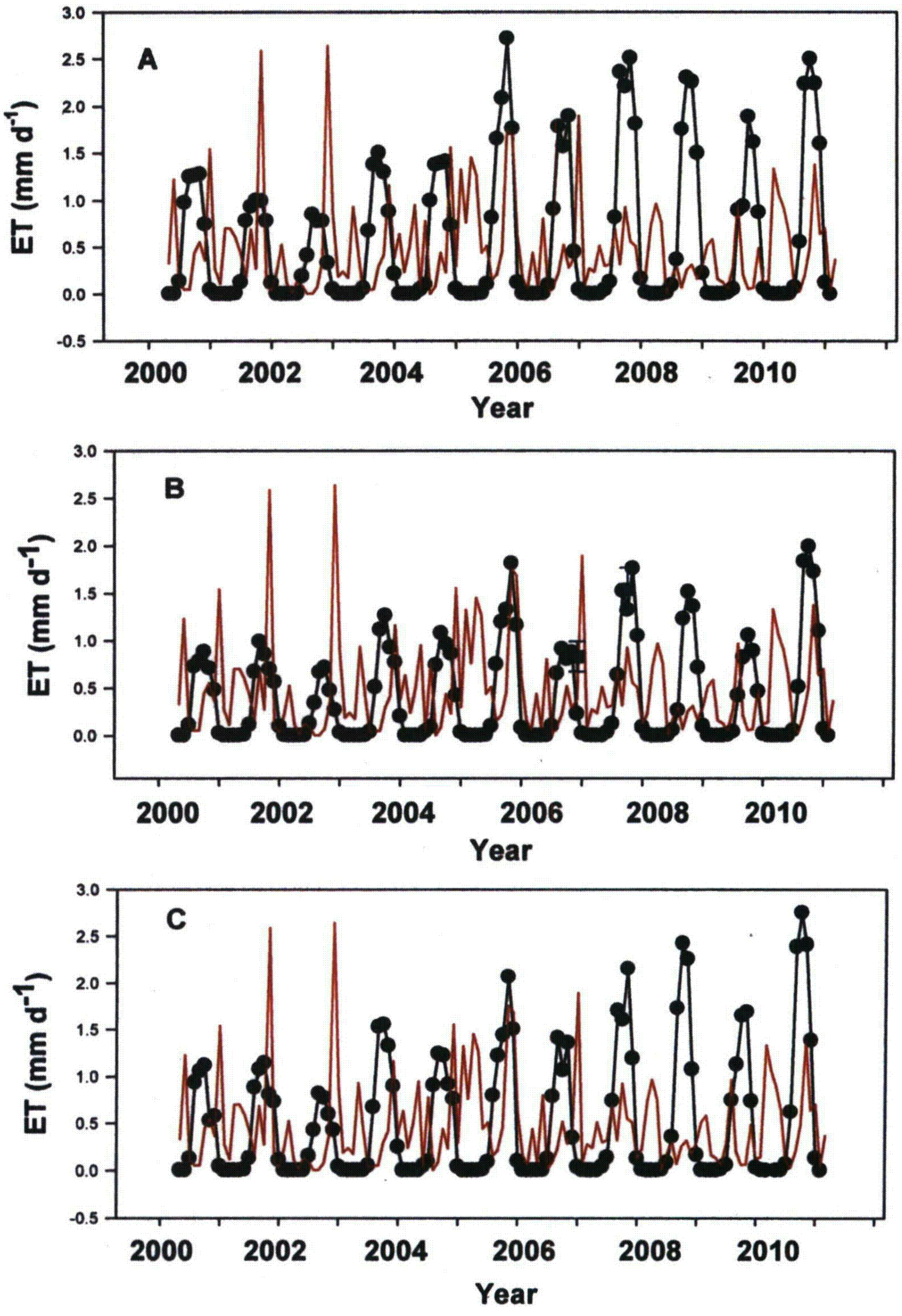


Figure F–5. ET in mm d^{-1} (black dots) estimated from MODIS Enhanced Vegetation Index and air temperature for the plants inside the source area fence (A); in the Outside ATCA zone (B); and in the Outside SAVE zone (C). The red lines are precipitation in mm d^{-1}. The inside-fence area was represented by four MODIS pixels encompassing 24 ha; the Outside SAVE area was represented by two MODIS pixels contained wholly within the area of interest; and the Outside ATCA area was represented by a rectangle of 4 × 5 pixels within the area of interest. Blue squares in (B) show ET measured by sap flow sensors in 2006 and 2007 and projected over the ATCA zone based on LAI and fractional cover.

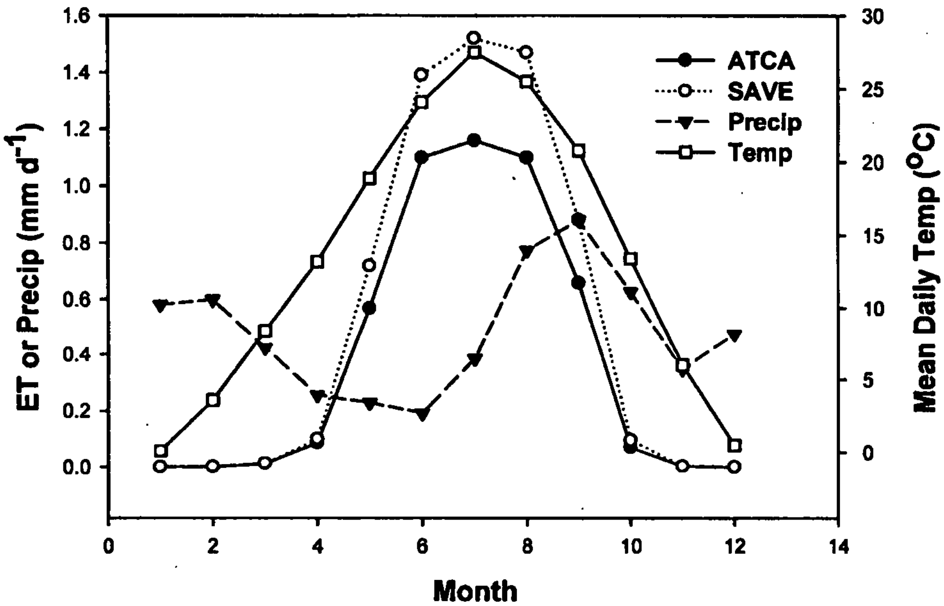


Figure F–6. Annual cycles of ET, precipitation, and air temperature in the Outside ATCA and Outside SAVE areas, averaged over years for 2000–2010.

Table F–2. Potential evapotranspiration (ET_o) and, precipitation, and ET estimated by MODIS satellite imagery for areas at the Monument Valley UMTRA site. Means and standard errors (SE) are shown for 2000–2004 and 2005–2010.

Year	ET_o	Precipitation	Estimated ET			
			Inside Fence	Outside SAVE	Outside ATCA	Whole Site
	mm year^{-1}					
2000	1573	168	189	146	123	144
2001	1499	214	145	149	122	136
2002	1482	143	103	99	99	90
2003	1508	146	183	191	147	169
2004	1461	212	185	159	129	146
Mean (SE)	1504 (19)	176 (17)	161 (17)	148 (15)	124 (8)	137 (13)
2005	1463	267	282	220	196	195
2006	1452	155	206	157	110	143
2007	1465	167	306	235	199	200
2008	1421	193	259	248	160	162
2009	1432	107	193	184	114	150
2010	1419	234	310	356	242	268
Mean (SE)	1442 (8)	187 (26)	259 (20)	233 (28)	170 (21)	186 (19)

Precipitation exceeded ET over all areas of the site from 2000 to 2004, suggesting that the site water balance favored recharge, which may be a factor in the expanding of the contamination plume. On the other hand, ET exceeded precipitation in the source area and in the SAVE stand outside the fence from 2005 to 2010. Irrigation water applied to 4 ha in the source area contributed an additional 60 mm yr^{-1} of water to the area represented by the 4 MODIS pixels

(24 ha) selected to represent the Inside Fence area; hence precipitation plus irrigation (247 mm yr^{-1}) approximately equaled ET (259 mm yr^{-1}) for this part of the site. This is expected, as there is no aquifer under most of the source area and the plants were dependent on precipitation and irrigation. On the other hand, black greasewood outside the fence could have been using groundwater as well as precipitation, because ET exceeded precipitation, and, in previous studies (McKeon et al. 2006; Jordon et al. 2008), plants over this part of the plume were shown to be extracting water from the alluvial aquifer based on stable isotope values.

F.5 Conclusion and Recommendations

The remote sensing method developed here for monitoring vegetation dynamics and ET at Monument Valley, using a combination of annual Quickbird images and 16-day MODIS images, should be accessible into the foreseeable future. Quickbird images are commercial products supplied by Digital Globe, Inc., which recently added another satellite, WorldView 2, to its fleet. Replacement satellites are also planned for NASA's Terra satellite, which acquires MODIS images.

The results suggest that from 2000 to 2010, the area over the plume appears to have switched from recharge to discharge of the aquifer. This could have important implications for the migration of contaminants away from the site. Increased vegetation cover and ET was due partly to revegetation projects conducted over the source area, and partly due to an observed decrease in grazing over the plume. Since vegetation dynamics and grazing pressure will continue to vary in the future, continued monitoring of the site by remote sensing is recommended.

Appendix G

Risk Evaluations

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The overall goal of Monument Valley pilot studies is to generate the science needed for sustainable protection of human health and the environment. The pilot studies focused on the contaminants of concern in the alluvial aquifer, nitrate, ammonium, and sulfate. The pilot studies revealed several natural processes that are acting to contain and remove these constituents from soil and groundwater, and the studies produced strong landscape-scale evidence that these processes can be enhanced and accelerated. As the pilot studies progressed, project scientists also considered whether enhancements might actually create risk to human health and the environment.

This section is a summary of evaluations of potential risks associated with plant uptake of contaminants, grazing of phytoremediation plantings by livestock, and constituents that may have caused soils to become stained over the course of the pilot studies, possibly as a result of soil ripping and irrigation.

G.1 Plant Uptake and Grazing

Project scientists conducted greenhouse, modeling, and field studies to evaluate uptake of soil and groundwater constituents and potential toxic effects for phytoremediation plants and for animals that might consume those plants. The toxicity studies focused on uranium, nitrogen, and sulfur, but also addressed other chemicals of concern.

G.1.1 Chemicals of Potential Concern

With respect to risks associated with plant uptake, project scientists were concerned primarily with accumulation of NO_3, SO_4, hydrocyanic acid, strontium, vanadium, uranium, and manganese within the plants, and how accumulation of these constituents could affect the quality of forage for livestock. A thorough discussion of potential toxic effects of these constituents is presented in an earlier phytoremediation report (DOE 2002). A summary follows.

Some plants accumulate hydrocyanic acid (HCN), commonly called prussic acid and a derivative of NO_3. HCN is usually not present in plants, but some plants can accumulate cyanogenetic glycoside. Plants that contain the glycoside have the potential to cause HCN toxicity when consumed by ruminants such as cattle and sheep. HCN interferes with the ability of oxygen to enter body cells thus causing suffocation at the cellular level (Strickland et al. 1995). In the Southwest, the plants most likely to cause HCN poisoning are sorghums. The potential is greatest for Johnson grass and the least for true sudan grasses. At Monument Valley, therefore, HCN poisoning of livestock would be of greatest concern if plume water were used to irrigate sorghums. The accumulation of nitrate is also of concern when feeding livestock. High nitrate accumulation in plant tissues also results in oxygen deprivation. But again, this would be of greatest concern only if plume water were used to irrigate sorghums.

Sulfur (S) toxicity could theoretically occur in livestock if levels are high enough for microflora to convert S to hydrogen sulfide in the gastrointestinal tract. However, it takes large amounts of S to start producing hydrogen sulfide. There are no established limits on S/SO_4 for cattle and sheep diets. An apparent maximum tolerable level for sheep is 0.4 percent dietary S as sodium sulfate (Subcommittee on Mineral Toxicity in Animals 1980).

Strontium (Sr) is an alkaline earth metal closely related to calcium (Ca). Strontium is processed in plants and animals similarly to Ca but the processing is less efficient. The effects of Sr on livestock are more pronounced when there are small concentrations of Ca present. Young animals fed small Ca and large Sr concentrations develop "strontium rickets," which affects bone growth (Colvin and Creger 1967). Assuming that animals have adequate Ca in their diet, plants containing up to 2,000 µg Sr g^{-1} can be tolerated (Subcommittee on Mineral Toxicity in Animals 1980).

Manganese (Mn) is an essential element for both plant and animal growth. However, Mn toxicity can result as an interference with iron causing a decreased production of hemoglobin. Sheep and cattle should not be fed diets containing more than 1,000 µg Mn g^{-1} (Subcommittee on Mineral Toxicity in Animals 1980).

Vanadium (V) has also been shown to be an essential element in animal diets, but can also be toxic by inhibiting enzymes and causing the lysis of cells. However, there is no established maximum tolerable limit for V (Subcommittee on Mineral Toxicity in Animals 1980).

Uranium (U) has been shown to be essential in small amounts for plant growth but not essential for animal growth. Toxicity to animals by U occurs in the kidney due to cell damage. Most animals do not absorb large amounts of U through digestion and there is little data on feeding U to farm animals. A safe concentration of dietary U for rats appears to be 400 mg U kg^{-1} (Subcommittee on Mineral Toxicity in Animals 1980).

G.1.2 Greenhouse Studies

Greenhouse studies were conducted at the University of Arizona primarily to evaluate varieties of sudan grass for hay production. Scientists evaluated varieties of sudan grass as an early candidate for the phytoremediation land farm (Appendix E). The studies used soil and water from the site to assess the feasibility of growing crop plants of forage quality (DOE 2002). A previous greenhouse study conducted with soil and water from a different uranium mill tailings site found this to be a feasible approach (Baumgartner et al. 2000a, 2000b).

Five types of crop plants were evaluated in the greenhouse: alfalfa, sudan grass, Sweet sudan grass, Sorghum-sudan grass, and the fourwing saltbush. The selection of crops was based on a literature search on the effects of high-nitrate irrigation water, on guidance from the DOE client, and on the suitability of land at Monument Valley for growing irrigated crops. The study used soils from the source area and from north of the source area, the proposed location for the land-farm study (Appendix E). Irrigation water treatments included 1,000, 500, and 83 mg/L NO_3 from wells 648, 777, and 778, respectively.

The best plant growth occurred on soil from north of the source area where the land-farm study was eventually conducted. Plant growth was inhibited in soils from the tailings pile footprint. Growth on all three soils improved with the addition of organic matter.

One thousand mg/L nitrate (measured as NO_3) in water was lethal to most plants. This toxicity was alleviated by the addition of organic matter to the soil. One thousand and 500 mg/L NO_3 in water resulted in plant tissue concentrations of NO_3 above recommended feeding values for cattle. At 83 mg/L NO_3 in the water, alfalfa did not accumulate NO_3 to excessive levels. All other plant types accumulated nitrate close to or above 5,000 mg/kg NO_3, the highest amount of nitrate considered safe for feeding ruminants. Plants grown with organic matter and watered with 1,000 mg/L NO_3 accumulated NO_3 up to 20 times the safe feeding level. HCN accumulation was lowest in Piper sudan grass with a mean below the lower toxic limit. Both Sweet sudan grass and Sorghum-sudan grass accumulated HCN above toxic levels. Sulfur as sulfate (SO_4) in dried plant tissues accumulated to harmful concentrations in alfalfa grown with water containing 83 mg/L NO_3 and 620 mg/L SO_4. Plants did not accumulate Sr, Mn, V, or U to harmful levels.

The main conclusion of the study was that alfalfa would be a better choice for hay production because sudan grass is more likely to accumulate toxic amounts of HCN and NO_3. Fourwing saltbush could also be grown as a hay crop or for grazing. However, because fourwing saltbush can accumulate nitrate, at least on the basis of this greenhouse study, a seed crop may be a more acceptable alternative because it would help alleviate toxicity concerns. Fourwing saltbush would be safe for short duration grazing if irrigated with plume water.

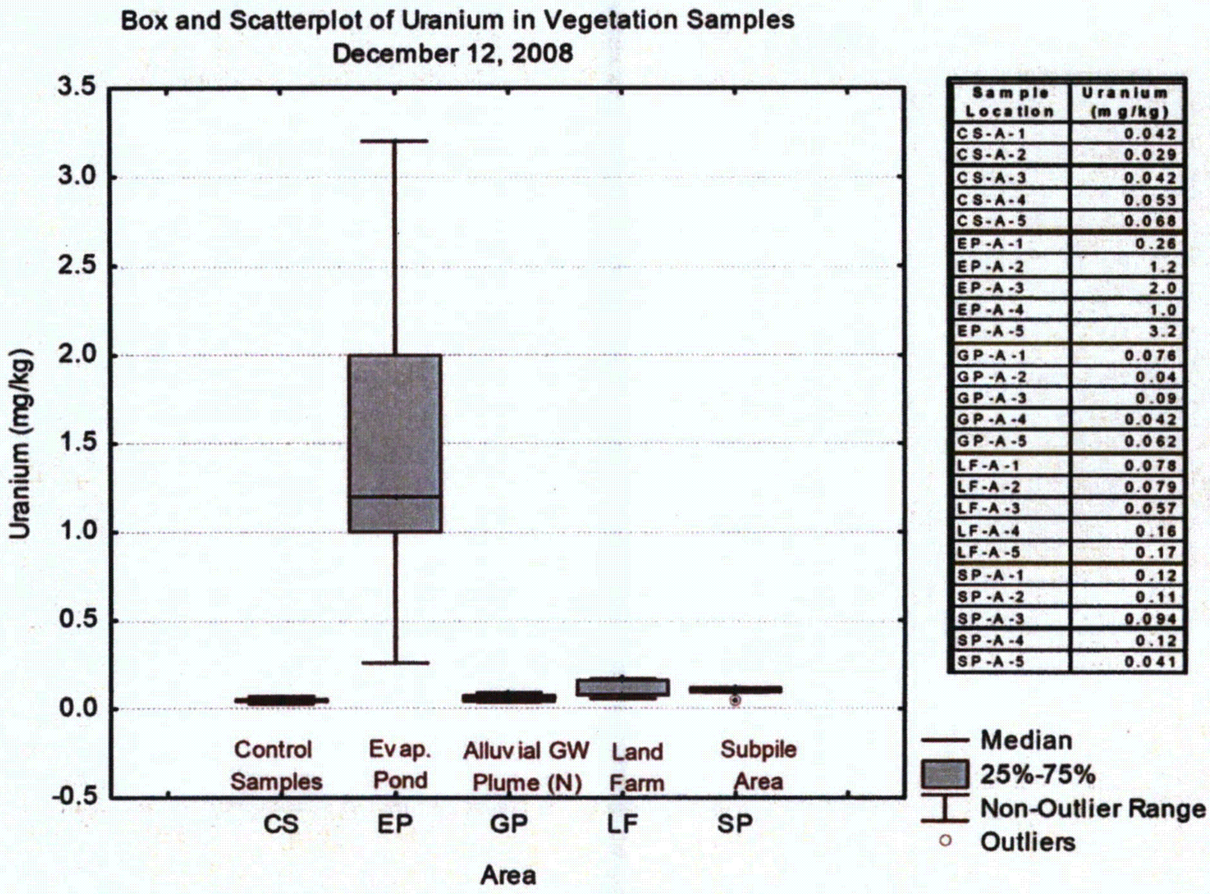
G.1.3 Field Studies of Plant Uptake

Field studies of plant tissue accumulation of nitrogen and uranium provide some information on possible toxicity if phytoremediation plantings were to be grazed continuously by livestock. This section is a summary of the field studies.

Nitrate toxicity is sometimes a problem for livestock (Sections G.1.1 and G.1.2). However, nitrate is the primary form of nitrogen, a plant nutrient, and is a normal constituent of plants. Whether nitrate accumulates in plants to toxic levels depends on the rate of uptake from the soil and the rate that plants convert it to nitrite, ammonia, and amino acids. As a rule, forage containing less than 5,000 ppm (0.5 percent) nitrate on a dry matter basis is safe. Project scientists determined total nitrogen content of plant tissues as part of the phytoremediation field study, but did not evaluate nitrate content. In the source area phytoremediation plantings, total nitrogen content of leaf and stem tissue ranged from 1.24 percent to 2.17 percent over 5 years, 2000–2005 (DOE 2006). If future land management were to include grazing, nitrate content of plant tissues would need to be determined.

Although most animals do not absorb large amounts of U through digestion and there is little data on U toxicity to farm animals, 400 mg kg^{-1} has been used as a safe dietary threshold (Section G.1.1). In 2008, project scientists sampled stem and leaf tissue for fourwing saltbush plants growing in different locations at Monument Valley. Five plants each were sampled in the source (subpile) planting, in the land-farm planting, in the Evaporation Pond planting, overlying the alluvial nitrate plume, and at a control site (an area south of the mill site that had not been disturbed by milling or remediation activities).

Results in Figure G–1 show that the highest concentrations of uranium were found in the former Evaporation Pond. The concentrations in vegetation samples from the former Evaporation Pond were similar to, and in some cases higher than, those found in evaporation pond soils. Concentrations of uranium in fourwing saltbush from all other areas were significantly lower and similar to the control samples. All uranium concentrations were over two orders of magnitude less than the stated dietary threshold.



Sample Location	Uranium (mg/kg)
CS-A-1	0.042
CS-A-2	0.029
CS-A-3	0.042
CS-A-4	0.053
CS-A-5	0.068
EP-A-1	0.26
EP-A-2	1.2
EP-A-3	2.0
EP-A-4	1.0
EP-A-5	3.2
GP-A-1	0.076
GP-A-2	0.04
GP-A-3	0.09
GP-A-4	0.042
GP-A-5	0.062
LF-A-1	0.078
LF-A-2	0.079
LF-A-3	0.057
LF-A-4	0.16
LF-A-5	0.17
SP-A-1	0.12
SP-A-2	0.11
SP-A-3	0.094
SP-A-4	0.12
SP-A-5	0.041

Figure G–1. Box and scatter plot of uranium (mg kg^{-1} dry weight) in tissue samples of fourwing saltbush growing in different locations at Monument Valley (DOE 2010).

G.2 Evaluation of Stained Soils

At different times during the course of the pilot studies, project scientists observed colored or "stained" soils in the source area plantings. This section is a summary of investigations concerning the potential toxicity of stained soils to plants and to humans.

G.2.1 Stained Subpile Soils

Project scientists have observed poor plant growth in the western part of the subpile planting since 1999. Satellite images show this area of poor growth as a whitish stain (Figure G–2). Previous analyses of soil samples from areas with both poor and good growth suggested that nitrate, sulfate, calcium, magnesium, strontium, and vanadium were higher in the poor-growth areas. Concentrations of iron, manganese, phosphate, potassium, sodium, and uranium were significantly lower in the poor-growth areas. Therefore, stunted growth of fourwing saltbush shrubs may be due to the combined effects of both an excess and a deficiency of several ions. In a previous greenhouse study, growth of sudan grass in soil obtained from a poor-growth area was significantly less than growth in a soil sample taken from a good-growth area. Chemical analysis of sudan grass tissue samples was inconclusive as to the causative agents of poor growth. Tests also found that soil bulk densities, another suspected cause of poor plant growth, were not significantly different in poor-growth and good-growth areas. A follow-up greenhouse study determined that moderate additions of iron and copper fertilizer improved plant survival but not growth.

Figure G–2. False-color 2009 Quickbird images showing whitish colored soil and areas of poor plant growth in the western portion of the subpile phytoremediation planting.

G.2.2 Manganese Toxicity Investigation

Parts of the subpile planting also have a shallow layer of black mottled material below the whitish soil surface in areas of stunted plant growth. Project scientists identified Mn and iron (Fe) concretions in samples from the mottled soil areas. They hypothesized that oxides of Mn at different oxidation states may have been deposited in the soil as a consequence of milling, and that these different oxidation states could be responsible for the "rainbow" appearance of colors around drip emitters in the stained areas. This section is a summary of a follow-up effort to determine the source of Mn concretions and to evaluate the potential health risks of Mn dust at the site (DOE 2009). The major findings follow:

- Chemical analyses of the concretions show that they are indeed aggregates enriched in Mn and Fe.
- Although the onset of irrigation may have mobilized Mn, and the Mn oxides may be precipitating, most of the mobilization of Mn at this site likely occurred during the leaching of uranium-rich minerals with acid.
- The levels of Mn are within values for normal soils, and they are well below any levels of concern for human health risks.

G.2.3 Evaporation Pond Crusts

In 2009, yellow- and green-colored deposits or soil crusts were noticed on the surface of the phytoremediation plantings in the Evaporation Pond. Sample analyses determined that the deposits were high in vanadium and uranium. In 2010, DOE conducted a radiological investigation, independent of the pilot studies, to evaluate the potential dose to workers resulting from exposure to radiological constituents in Evaporation Pond soils (DOE 2010). Highlights of the investigation follow:

- When the site was remediated between 1992 to 1994, all areas of the site, including the former Evaporation Pond, were verified clean under the UMTRCA surface soil cleanup standard of 5 pCi/g radium-226 (Ra-226) and the subsurface standard of 15 pCi/g. NRC approved the Monument Valley cleanup on April 5, 2001.
- Although the Evaporation Pond probably represents worst-case conditions in terms of contamination, post-cleanup verification studies, as corroborated by NRC, indicate that cleanup commitments were fulfilled.
- Because fourwing saltbush in the former Evaporation Pond had poor growth rates compared to other plantings, project scientists sampled yellow and green stains as a possible source of poor growth and determined that the stains had elevated levels of uranium and vanadium.
- As a best management practice, DOE conducted a radiological screening because of the higher-than-expected uranium results. Results indicated higher-than-anticipated gamma levels in the area.
- A follow-up soil sampling from the former Evaporation Pond found uranium-234 plus uranium-238 levels from 31 to 985 pCi/g. The ratio between uranium-234 and uranium-238 was consistently close to 1. The concentrations of thorium and radium were much lower than those of uranium, and the highest measured value for radium was less than 2 pCi/g.
- To ensure that workers have not been exposed to excessive dose levels from isotopic uranium in surface soils, risk calculations were performed. Risks were estimated using an allowable exposure rate of 25 millirems (mrem) per year, the highest measured results for the isotopes of uranium, and very conservative exposure assumptions. The results indicate that risks are well below the allowable exposure rate of 25 mrem per year.

Appendix H

Beneficial Land Use

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The Monument Valley pilot studies investigated potential beneficial land uses as part of an overall remedy. The contaminants of concern, nitrate and ammonium, are also the dominant sources of nitrogen in desert soil, an essential element for plant growth. Therefore, although seemingly a contradiction, nitrate and ammonium should be viewed both as contamination with respect to groundwater quality, but also as a resource with respect to plant nutrition and growth.

The levels of nitrogen in soil and groundwater at Monument Valley produce abundant foliage and seed growth. The phytoremediation plantings produce seed crops that the Navajo Nation could harvest for mine-land reclamation and rangeland restoration. Harvested seed may be worth $10,000 per acre. Fourwing saltbush is highly palatable to livestock and wildlife. Livestock grazing or harvesting saltbush foliage for hay, if managed correctly, could actually stimulate plant growth and enhance phytoremediation. Fourwing saltbush also has traditional, medicinal value to Native Americans.

An objective of the Monument Valley pilot studies is to evaluate options for exploiting nitrogen contamination to fertilize native plants for possible beneficial land reuse as seed and forage crops. This is possible because the primary contaminants of concern in the alluvial aquifer and in the plume source area soils are nitrate and ammonium. This section reviews the role nitrogen plays in rangeland ecosystems, and how nitrogen contamination at Monument Valley could be utilized to increase native plant forage and seed production.

H.1 Ecological Importance of Nitrate and Ammonium

An understanding of potential beneficial uses of nitrogen contamination must start with a review of the ecological role of nitrogen. Nitrogen is an essential element for plants—without it, there would be no life as we know it. Nitrogen is required for many important structural, genetic, and metabolic compounds in plant cells. Nitrogen is a major component of chlorophyll, the compound by which plants use sunlight energy to produce sugars from water and carbon dioxide—photosynthesis. It is also a major component of amino acids, the building blocks of proteins. Some proteins act as structural units in plant cells while others act as enzymes, making possible many of the biochemical reactions on which life is based. Nitrogen is a component of energy-transfer compounds, such as ATP (adenosine triphosphate), which allow cells to conserve and use the energy released in metabolism. Finally, nitrogen is a significant component of nucleic acids such as DNA, the genetic material that allows cells and whole plants to grow and reproduce.

Although nitrogen is one of the most abundant elements on earth, plant productivity in desert ecosystems is commonly limited by insufficient soil nitrogen (Whitford 2002). The most abundant form of nitrogen, gaseous nitrogen (N_2) molecules in the atmosphere, is not directly available to most plants that need it. Plant-available nitrogen exists primarily in soils as organic nitrogen compounds, ammonium ions (NH_4^+), and nitrate ions (NO_3^-). In desert ecosystems, the plant-available forms of nitrogen are inorganic ammonium and nitrate.

Typically, nitrogen reserves become depleted or altered in disturbed landscapes, such as at the Monument Valley site, because the healthy cycling of nitrogen through the ecosystem is inhibited or prevented. Restoration ecologists often apply nitrogen fertilizer under these conditions, in the form of ammonium or nitrate, to help jumpstart nitrogen cycling and enhance revegetation. Monument Valley is unique. At Monument Valley, elevated levels of ammonium and nitrate in soil and shallow groundwater can be viewed both as contamination with respect to groundwater quality, but also as a resource to be utilized with respect to plant nutrition and growth.

H.2 Land Reuse: Seed and Forage Crops

Atriplex canescens (fourwing saltbush) is one of the most widely distributed and important native shrubs on rangelands in the western United States including the Intermountain, Great Basin, and Great Plains regions. It is an important forage plant in western deserts of the United States and is widely used for reclamation of drastically disturbed lands and for rangeland restoration. Historically, fourwing saltbush has probably been the most seeded of all Western shrubs (Aldon 1972, Booth 1985). As a pioneer shrub it has proven useful for accelerating and directing plant succession on mined lands and degraded rangelands, especially when transplants are used (Glenn et al. 2001, Watson et al. 1995). The species comprises at least six distinct varieties that appear to be adapted to local soil and climate regimes (Glenn et al. 1996; Glenn and Brown 1997). For revegetation on Navajo mine lands, the diploid variety *angustifolia* was found to be better adapted for rapid establishment on disturbed sandy soils than the slower-growing variety *occidentalis*.

Phytoremediation plantings at Monument Valley produce fourwing saltbush seed crops annually that the Navajo Nation could harvest for mine-land reclamation and rangeland restoration (Waugh et al. 2010). As fertilizer, the nitrogen contamination has resulted in luxuriant growth of fourwing saltbush and abundant seed in the pilot study plantings (Figure H–1). In fall 2001, project scientists harvested about 50 kg of fourwing saltbush seed; about 2 kg or more of seed from each of several mature plants. There were about 4,000 plants in the subpile phytoremediation planting, half of which are female (fourwing saltbush are dioecious; separate male and female plants), so 2,000 plants × 2 kg gives a potential yield of 4,000 kg of seed. The field is 1.6 ha, so the potential yield is 2,500 kg/ha. Seed companies charge up to $66/kg ($30/lb) for seed with the wings milled off. If the seed companies pay as little as $10/kg ($4.50/lb) for bulk seed, this would be a return of $25,000/ha (about $10,000/acre). Saltbush seeds are harvested by stripping or beating the ripe fruits into shoulder hoppers, boxes, or bags, or onto tarps spread under the bushes. Vacuum or reel type harvesters may also be used (McArthur et al. 2004).

Fourwing saltbush is also highly palatable browse for most livestock and big game and could be managed for grazing or harvesting. It is palatable to cattle, sheep, and deer throughout the growing season, and provides nutritious winter browse on many areas as a fall and winter browse plant for bighorn sheep, antelope, and elk. With minimal toxicity risks (Appendix G), Monument Valley fourwing saltbush plantings could be made available for livestock belonging to local residents. The plantings would need to be closely managed for short duration grazing in the winter to maintain plant health. Plants continuously browsed by cattle usually develop a hedged form and produce relatively little growth. Managed grazing may actually improve phytoremediation capacity. Moderate browsing by livestock for short durations can significantly stimulate fourwing saltbush growth, whereas plants protected from browsing for a year or more respond with progressively less leader production as length of protection time increases (Price et al. 1989). Fourwing saltbush can also be cut and windrowed with a hay-swather and then combine-harvested for seed or fodder (Carlson et al. 1984).

Figure H–1. Seed production (light green) of fourwing saltbush transplants in the source area phytoremediation planting at Monument Valley, September 22, 2010.

H.3 Ethnobotany

Fourwing saltbush also has traditional, medicinal value for Native Americans (Moerman 2009). Among other traditional uses, Native Americans boil fresh fourwing saltbush roots with a little salt and drink half-cupful doses for stomach pain and as a laxative. Roots are ground and applied as a toothache remedy. Leaf or root tea is taken as an emetic for stomach pain and bad coughs. Soapy lather from leaves is used for itching and rashes from chickenpox or measles. Fresh leaf or a poultice of fresh or dried flowers is applied to ant bites. Leaves are used as a snuff for nasal problems. Smoke from burning leaves is used to revive someone who is injured, weak, or feeling faint.

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Appendix I

List of Publications, Reports, and Presentations

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LM funded the pilot studies at the Monument Valley site to gain the knowledge (science) and tools (technology) as a basis for informed, efficient, and cost-effective remediation strategies for the alluvial aquifer and subpile soils. By publishing, LM subjected the pilot studies to scholarly scrutiny by independent communities of experts in these fields of research; this process is known as refereeing. Publishing provides a measure of credibility and enables others to utilize these contributions to the science and technology of enhanced natural attenuation. Listed below are a book chapter and peer-reviewed pilot study publications in scientific journals and symposia proceedings followed by lists of DOE reports and technical presentations. The full-text journal articles are available on request.

Book Chapter

Waugh, W.J., E.P. Glenn, P.H. Charley, B. Maxwell, and M.K. O'Neill, 2011. *Helping Mother Earth Heal: Diné College and Enhanced Natural Attenuation Research at U.S. Department of Energy Uranium Processing Sites on Navajo Land*, In: Burger, J. (ed.) Stakeholders and Scientists: Achieving Implementable Solutions to Energy and Environmental Issues, Springer, New York, New York.

Journal and Proceedings Publications

Bresloff, C.J., U. Nguyen, E.P. Glenn, W.J. Waugh, and P.L. Nagler (draft), *Remote Sensing Monitoring of Site Vegetation and Evapotranspiration by a Desert Phreatophyte Community at a Former Uranium Mill Site on the Colorado Plateau.*

Borden, A.K., M.L. Brusseau, K.C. Carroll, N. H. Akyol, A. McMillan, J. Berkompas, Z. Miao, F. Jordan, G. Tick, W.J. Waugh, and E.P. Glenn, 2011. *Ethanol addition for enhancing denitrification at the uranium mill tailings site in Monument Valley, Arizona.* Water, Air, and Soil Pollution DOI 10.1007/s11270-011-0899-1.

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Technical Conference Presentations

Waugh, W.J., and E.P. Glenn, 2012. *Land-Farm Phytoremediation of Groundwater Using Native Desert Shrubs at the Monument Valley, Arizona, DOE Legacy Waste Site*, Proceedings of Waste Management 2012.

McMillan, A.L., A.K. Borden, M.L. Brusseau, K.C. Carroll, N.H. Akyol, J.L. Berkompas, Z. Miao, F. Jordan, G.R. Tick, W.J. Waugh, and E.P. Glenn, 2011. *Long-term effects of ethanol addition on denitrification at the uranium mill tailing site in Monument Valley, Arizona,* Proceedings of the American Geophysical Union Fall Meeting, San Francisco, California, December 5–9.

Borden, A.K., J. Berkompas, Z. Miao, K.C. Carroll, W.J. Waugh, E.P. Glenn, and M.L. Brusseau, 2009. Pilot Tests of Enhanced Denitrification Using Ethanol, *Geological Society of America Annual Meeting*, Portland, Oregon, October 21.

Carroll, K.C., F.L. Jordan, E.P. Glenn, W.J. Waugh, and M.L. Brusseau, 2008. *Comparison of Nitrate Attenuation Characterization Methods for Groundwater Remediation* (poster), American Geophysical Union Annual Meeting, San Francisco, California, December 15–19.

Jordan, F., J. Waugh, and E. Glenn, 2008. *A Plant-Based Approach to Remediating a Nitrate-Contaminated Soil/Aquifer System in a Desert Environment*, 2008 Joint Meeting of The Geological Society of America and Soil Science Society of America, Houston, Texas, October 5–9.

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Appendix J

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April 28, 2014

Mr. Richard Bush
U.S. Department of Energy
Office of Legacy Management
2597 Legacy Way
Grand Junction, CO 81503

SUBJECT: U.S. NUCLEAR REGULATORY COMMISSION STAFF REVIEW OF U.S. DEPARTMENT OF ENERGY REPORT ENTITLED "MONITORED NATURAL AND ENHANCED ATTENUATION OF THE ALLUVIAL AQUIFER AND SUBPILE SOILS AT THE MONUMENT VALLEY, ARIZONA SITE: FINAL PILOT STUDY REPORT, APRIL 2013" (DOCKET NUMBER WM-00070)

Dear Mr. Bush:

On June 6, 2013, the U.S. Department of Energy (DOE) provided the U.S. Nuclear Regulatory Commission (NRC) staff with the final report entitled "Monitored Natural and Enhanced Attenuation of the Alluvial Aquifer and Subpile Soils at the Monument Valley, Arizona Site: Final Pilot Study Report, April 2013" (Agencywide Document Access and Management System (ADAMS) Accession Number ML13164A278). This report provides the results of DOE's pilot study to determine the viability and practicality of natural and enhanced attenuation for remediating ammonium, nitrate and sulfate in the subpile soils and alluvial aquifer at the Monument Valley Uranium Mill Tailings Radiation Control Act site. The results of this study will be used by the DOE to help develop compliance strategies for a Ground Water Compliance Action Plan for the Monument Valley site.

The NRC staff worked with the Center for Nuclear Waste Regulatory Analysis (CNWRA) to evaluate the findings in the DOE pilot study report. The results of the CNWRA's and NRC staff's evaluation are summarized in the enclosed report. If you have any questions concerning the evaluation, please contact me at 301-415-6749 or email at Dominick.Orlando@nrc.gov.

In accordance with 10 CFR 2.390 of the NRC's "Agency Rules of Practice and Procedure," a copy of this letter will be available electronically for public inspection in the NRC Public

Document Room or from the Publicly Available Records component of NRC's ADAMS. ADAMS is accessible from the NRC Web site at http://www.nrc.gov/reading-rm/adams.html.

Sincerely,

/RA/
Dominick A. Orlando, Senior Project Manager
Materials Decommissioning Branch
Decommissioning and Uranium Recovery
Licensing Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

Enclosure:
Evaluation of Final Phytoremediation
Pilot Study

Docket No. WM-00070

cc: A. Gill, DOE/LM
M. Roanhorse, NNAML Reclamation

MONITORED NATURAL AND ENHANCED ATTENUATION OF THE ALLUVIAL AQUIFER AND SUBPILE SOILS AT THE MONUMENT VALLEY, ARIZONA, PROCESSING SITE: REVIEW OF FINAL STUDY REPORT

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1 SUMMARY OF ENVIRONMENTAL ASSESSMENT COMPLIANCE GOALS AND COMPLIANCE STRATEGY

Congress passed the Uranium Mill Tailings Radiation Control Act (UMTRCA) in 1978 to control and mitigate risks to the environment and human health from sites involved in processing uranium ore. The U.S. Department of Energy (DOE) was directed to conduct remedial actions at 24 inactive uranium-ore processing sites. The selection and performance of the remedial actions required full participation by states, in consultation with affected American Indian Tribes, and with the concurrence of the U.S. Nuclear Regulatory Commission (NRC). This report reviews the results of pilot studies by DOE's Office of Legacy Management performed at the uranium-ore processing site at Monument Valley, Arizona. The site is within the Navajo Nation and was included in UMTRCA as one of the 24 inactive uranium-ore processing sites. The pilot studies evaluated several approaches to remediating ammonium (NH_4^+), nitrate (NO_3^{-1}), and sulfate (SO_4^{-2}) remaining at the site following removal of tailings and other residual radioactive materials on or near the ground surface. Uranium is present in small quantities deeper in the alluvial aquifer but was not included in the pilot studies. DOE may use the results of the pilot studies to evaluate and propose final compliance strategies and remedial actions for contamination in the soils and alluvial aquifer at the site. According to DOE (2013), which we will hereafter call the Pilot Study Report, the pilot studies were carried out pursuant to the following objectives and scope for pilot studies presented in DOE (2004), which we will hereafter call the Work Plan, and the associated environmental assessment (DOE, 2005):

- Delineate extent of nitrate, ammonium, and sulfate in subpile soils
- Investigate presence and mobility of natural nitrate and sulfate sources
- Determine causes of stunted plant growth and recourse
- Expand irrigated planting of *Atriplex canescens*
- Quantify effects of irrigation on microbial denitrification processes and rates
- Investigate nitrification processes, rates, and possible enhancements

The objectives of the pilot studies were restated in the Work Plan and DOE (2005):

- Estimate the total capacity of natural chemical and biological processes that are reducing concentrations of groundwater contaminants at the site.

- Investigate methods to enhance and sustain attenuation processes that could be implemented if the total capacity of natural processes is inadequate.

- Demonstrate methods for (i) characterizing attenuation rates, (ii) verifying short-term results, and (iii) monitoring performance of natural attenuation processes and enhancements.

- Evaluate land farming as an active remediation option if natural and enhanced attenuation processes are both inadequate.

The objectives of the Pilot Study Report differ somewhat from those stated in the Work Plan, possibly because DOE's understanding of the environmental processes at the site has evolved since the Work Plan was written. The results of the pilot studies are intended to support the decision points in the decision framework for compliance strategies presented in DOE (2005) and reproduced in Figure 1-1. The maximum concentration limits (MCLs) mentioned in

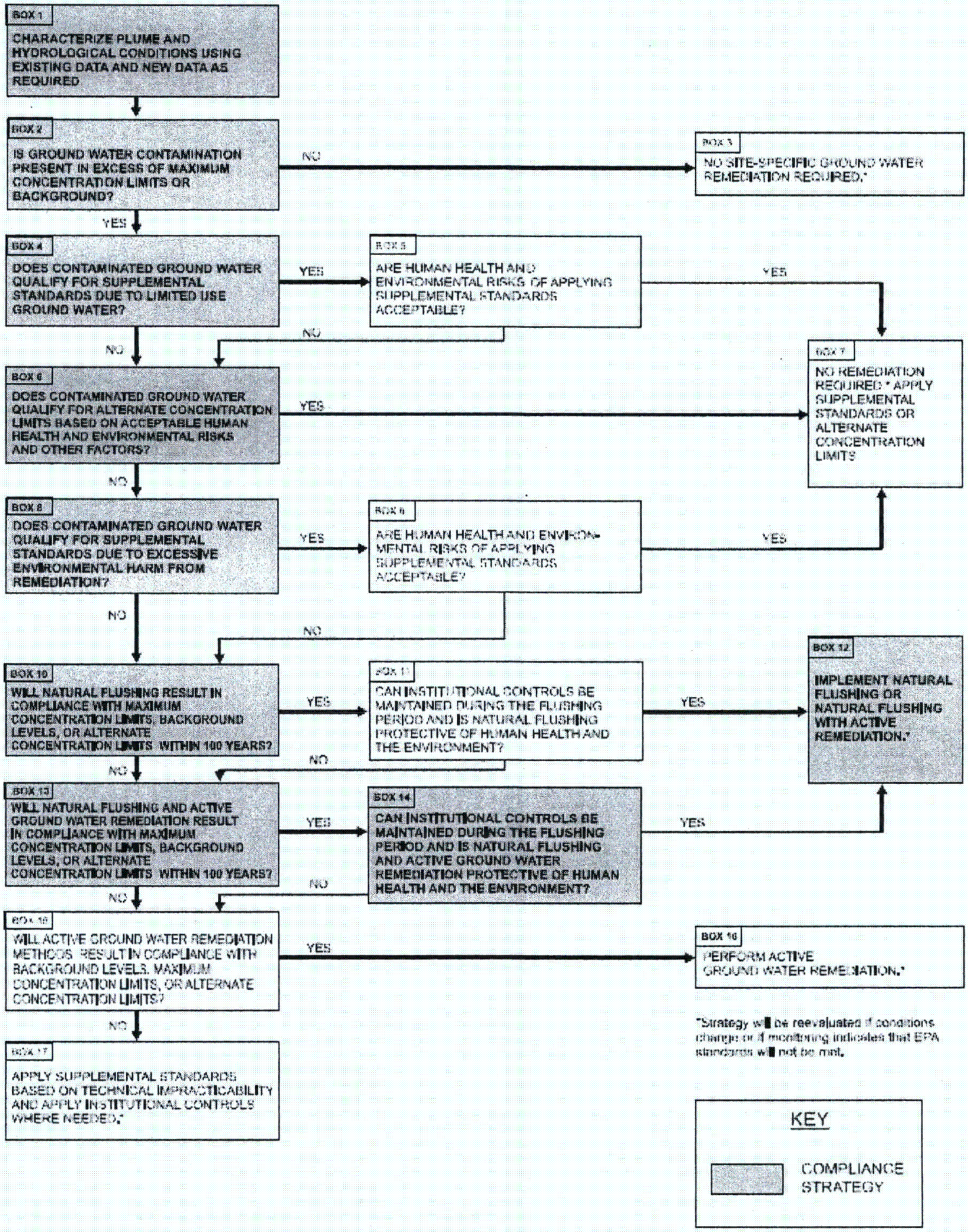

Figure 1-1. Compliance Selection Framework for the Alluvial Aquifer at the Monument Valley Site (Reproduced From DOE, 2005)

Figure 1-1, Boxes 10 and 13, are the U.S. Environmental Protection Agency (EPA) MCLs for nitrate as NO_3^{-1} [44 milligrams per liter (mg/L)][44 parts per million (ppm)] and uranium (0.044 mg/L) [0.044 ppm]. According to DOE, "DOE will use best efforts to comply with the Navajo Nation remediation goal of 250 mg/L for sulfate" (DOE, 2005). DOE's proposed actions for ammonium, nitrate, and sulfate at the Monument Valley Site are summarized in Figure 1-2. In its studies, DOE considered three zones: subpile soils, shallow alluvial aquifer, and deep alluvial aquifer. The pilot studies reviewed in this report pertain only to remediation of ammonium, nitrate, and sulfate. Ammonium in subpile soils is a potential source of nitrate in the alluvial aquifer. The pilot studies are summarized in Figure 1-3.

Aquifer	Area	Contaminants To Be Monitored	Compliance Strategy	Rationale
Alluvial	Subpile soils	Ammonium, Nitrate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of ammonium that could be a continuing source of nitrate contamination in the alluvial aquifer
	Shallow portions of aquifer	Nitrate, sulfate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of nitrate and sulfate
	Deeper portions of aquifer	Nitrate, sulfate	Passive remediation (combination of natural flushing and land farming)	Reduce concentrations of nitrate and sulfate
		Uranium	Passive remediation (natural flushing)	Uranium contamination does not appear to be widespread, although anomalous elevated concentrations have recently been detected.
De Chelly	Isolated area	Uranium	Passive remediation (natural flushing)	Uranium concentration only slightly exceeds the MCL in an isolated area and is decreasing with time. There is no current human health or ecological risk.

MCL = maximum concentration limit established in 40 CFR 192.

Figure 1-2. Summary of DOE's Proposed Actions in the Alluvial Aquifer (Reproduced From DOE, 2005)

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports[a])
1. Control Subpile Soil Water Balance and Percolation	Enhance native vegetation establishment and evapotranspiration (ET) on source area soils to control the soil water balance, limit deep percolation, and prevent continued leaching of nitrate and ammonium into the alluvial aquifer.	1. Determined extent of subpile ammonium and nitrate. 2. Expanded subpile phytoremediation planting and irrigation system. 3. Investigated natural sources of vadose zone nitrate. 4. Monitored soil water content and percolation flux. 5. Monitored plant growth and related evapotranspiration. 6. Investigated causes and recourses for area of stunted plant growth.
2. Enhance Natural Attenuation in the Subpile Soils	Remove nitrate and ammonium from subpile soils by enhancing natural phytoremediation and bioremediation.	1. Monitored plant growth and related nitrogen uptake. 2. Sampled plant root abundance and distribution. 3. Sampled soil organic carbon. 4. Monitored changes in subpile soil ammonium and nitrate. 5. Evaluated natural and enhanced microbial denitrification. 6. Evaluated soil nitrification processes.
3. Evaluate Natural and Enhanced Phytoremediation of the Alluvial Aquifer	Evaluate and enhance natural phytoremediation by native phreatophytes rooted in the plume to remove plume nitrogen and, by increasing transpiration, to hydraulically limit the continued spread of the plume.	1. Evaluated historical modeling and monitoring of nitrate, ammonia, and sulfate in the alluvial aquifer. 2. Investigated rooting depths of native phreatophytes. 3. Evaluated phreatophyte transpiration and hydraulic control. 4. Evaluated effects of grazing management and revegetation on phytoremediation capacity for nitrogen uptake and transpiration. 5. Developed a remote sensing protocol to monitor natural and enhanced phytoremediation.
4. Evaluate Natural and Enhanced Denitrification in the Alluvial Aquifer	Characterize natural attenuation processes acting to reduce contaminant levels in the alluvial aquifer and investigate options for enhancing denitrification.	1. Investigated natural concentrations of alluvial nitrogen. 2. Modeled plume dynamics and natural attenuation processes. 3. Estimated natural denitrification in the alluvial aquifer based on nitrate concentrations and nitrogen isotope fractionation. 4. Evaluated carbon sources to enhance aquifer denitrification using laboratory microcosm assays. 5. Conducted field tests of the denitrification capacity and dispersion of ethanol injected into the alluvial aquifer.
5. Evaluate Land-Farm Phytoremediation	Evaluate land-farm phytoremediation, an active remedy alternative that involves pumping and irrigating a crop of native plants with nitrate-contaminated groundwater.	1. Conducted a feasibility study of land-farm phytoremediation. 2. Designed and constructed a land farm experiment to evaluate effects of different native shrub crops and irrigation nitrate levels on plant health, soil water, and soil nitrogen. 3. Characterized baseline physical and chemical properties of land-farm soils. 4. Monitored soil water content profiles using neutron hydroprobes. 5. Sampled for changes in soil nitrate and ammonium profiles. 6. Monitored crop health and growth using remote sensing.

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports[a])
6. Reduce Sulfate Levels as Possible	To the extent that is practical, reduce sulfate concentrations in the alluvial aquifer and sequester as soil sulfate in concert with remedies developed for groundwater nitrogen contamination.	1. Evaluated natural sources of sulfate in the alluvial aquifer. 2. Evaluated plant uptake of sulfate in subpile soils and alluvial aquifer. 3. Monitored changes in subpile soil sulfate profiles. 4. Monitored effects of ethanol injection into the alluvial aquifer on sulfate reduction. 5. Investigated gypsiferous soils as an analog of sulfate sequestration in a phytoremediation land farm. 6. Measured sequestration of sulfate in land farm soils.
Evaluate Potential Risks	Evaluate potential risks to human health and the environment related to the pilot studies and possible remedies.	1. Evaluated risks of plant uptake and livestock grazing for chemicals of potential concern in the subpile soil and groundwater. 2. Evaluated potential phytotoxicity of stained or colored subpile soils. 3. Investigated the potential health effects of manganese concretions in the subpile soils. 4. Conducted a radiological investigation of yellow crusts on the soil surface for the phytoremediation planting in the Evaporation Pond.

Figure 1-3. Pilot Studies Titles, Objectives, and Scope (Reproduced From the Pilot Study Report, Table 1-3)

2 SUMMARY OF SIGNIFICANT CLAIMS IN THE FINAL STUDY REPORT RELATED TO COMPLIANCE GOALS

2.1 Subpile Soils

The subpile soils at the Monument Valley processing site were assumed by DOE to be sources of ammonium, nitrate, and sulfate that could contaminate the alluvial aquifer at the site. Because nitrate and sulfate are anions, they can be readily transported downward through soils to underlying aquifers by meteoric water. Ammonium is a cation and tends to be less mobile because it is retarded by the electrical field around net negatively charged soil particles. Ammonium in soils, however, can be converted to nitrate by a process called nitrification in which ammonium cations are converted to nitrate anions by microorganisms. The aerobic process commonly occurs in soils because the microorganisms that cause the nitrification are ubiquitous in most soils. Hence, the ammonium in soils can be a source of nitrate contamination in underlying aquifers.

DOE investigated passive remediation approaches (natural and enhanced phytoremediation) to minimize additional nitrate and sulfate contamination of the alluvial aquifer from the subpile soils as compliance strategies for meeting EPA standards and the Navajo Nation remediation goals. DOE conducted preliminary phytoremediation feasibility studies (DOE, 2002) to evaluate whether natural and enhanced phytoremediation would be viable options for reducing nitrate concentrations in the alluvial aquifer at the Monument Valley Site. The results indicated that natural and enhanced phytoremediation would be viable options and would be consistent with the revegetation and land management goals of the site. DOE defined natural phytoremediation as relying on existing plants on the site for the alluvial aquifer remediation and defined enhanced phytoremediation as actions that include planting of additional plants, supplying irrigation, or providing fertilization, or other activities that would increase the health and number of plants that would contribute to the alluvial aquifer remediation. In general, DOE uses enhanced phytoremediation and enhanced denitrification to mean that natural processes at the Monument Valley site are being manipulated by human intervention to increase or accelerate contaminant attenuation beyond what occurs without the intervention (page A–16 of Appendix A of the Pilot Study Report).

Additional pilot studies were conducted pursuant to the Work Plan and the associated environmental assessment (DOE, 2005). The studies were conducted to evaluate the proposed compliance strategies in greater detail than the preliminary feasibility studies. For subpile soils, the focus was on (i) using phytoremediation to control the downward movement of water, (ii) enhancing natural nitrate attenuation by microorganisms, and (iii) reducing sulfate concentrations. In addition, the studies were designed to assess the distribution of ammonium, nitrate, and sulfate in the subpile soils as well as the soil water content. The Pilot Study Report makes the following conclusions regarding the effectiveness of the potential compliance strategies.

2.1.1 Water Balance Using Enhanced Phytoremediation

An established mixture of native plants can transpire sufficient water from the subpile soils to prevent the downward migration of water, which would prevent leaching of ammonium, nitrate, and sulfate into the alluvial aquifer. To establish mature native plants [fourwing saltbush (*Atriplex canescens*) and black greasewood (*Sarcobatus vermiculatus*)], transplanting and irrigation was necessary. Irrigation was supplied at a rate less than plants could transpire (i.e., deficit irrigation). Fencing was used to restrict grazing animals from the plots. However, grazing was simulated by periodic cutting of the plants. DOE concluded that the resulting healthy community of vegetation was able to utilize available water in the subpile soils and prevent downward water movement to the alluvial aquifer. Measurements of water content and flux were used to support their conclusion.

2.1.2 Enhanced Denitrification in the Vadose Zone

The increased soil water content as a result of deficit irrigation yielded enhanced denitrification in the subpile soils. Approximately half of the soil nitrogen was removed during 2000–2010. Because only a small quantity of nitrogen and sulfur was in the plants and the soil nitrogen was enriched with ^{15}N, it was hypothesized that soil microorganisms were mainly responsible for the reduction in nitrogen content. It was noted that soil bacteria preferentially utilize ^{14}N versus ^{15}N in their metabolism during denitrification. Therefore, an enrichment of ^{15}N suggests that denitrification is ongoing. This also was supported by nitrous oxide production that was 10 to 20 times higher in assay chambers placed over irrigated versus nonirrigated soils. Nitrous oxide is a product from denitrification. To further enhance denitrification, a carbon source (ethanol) was added to the irrigation water to support microbial growth.

2.1.3 Treatment of Sulfate in Vadose Zone

Phytoremediation in the subpile soils is reducing the sulfate transport to the alluvial aquifer because of the induced water balance. In addition, the plants will take up sulfate into their tissues and retard the downward migration of sulfate. Furthermore, sulfate may precipitate as gypsum (hydrated calcium sulfate) and remain in the subpile soils.

2.2 Alluvial Aquifer

The Pilot Study Report describes potential remediation actions for the shallow alluvial aquifer {water table less than approximately 15 meters (m) [50 feet (ft)} below land surface) and deep alluvial aquifer {water table greater than approximately 15 m [50 ft] below land surface}. Some of the remedial actions addressed by the pilot studies pertain to just the shallow portion of the aquifers, while others would apply to both portions. The basis for distinguishing the shallow and deep portions of the alluvial aquifer is the assumed maximum root depth of phreatophytes being approximately 15 m [50 ft]. DOE's claims and conclusions based on the results of the pilot studies are contained in the Pilot Study Report, Table 4.

2.2.1 Hydraulic Control of Plume by Phreatophyte Evapotranspiration

Native phreatophytes transpired water from the shallow alluvial aquifer and "hydraulically slowed plume dispersion" (Pilot Study Report, Table 4, p. 26]. DOE appears to base this interpretation on the conclusion that phreatophytes are removing water from the shallow aquifer. DOE also concluded that "[-]evegetation of denuded areas and management of grazing in other areas overlying the plume would greatly increase transpiration, enhancing hydraulic control." The conclusion that phreatophytes are removing water from the aquifer is based on

- The physiology of the native vegetation consisting of phreatophytic shrubs, fourwing saltbush, and black greasewood (Pilot Study Report, Appendix C, Section C.1)

- The stable hydrogen and oxygen isotopic signatures of phreatophyte plant matter being similar to that in the deep vadose zone and top of the water table (Pilot Study Report, Appendix C, Section C.1.2)
- The measured evapotranspiration rates of phreatophytes at the site (Pilot Study Report, Appendix C, Section C.1.5

2.2.2 Phytoremediation of the Nitrate and Sulfate

The rate of direct uptake by phreatophytes of nitrate and sulfate from the alluvial aquifer was very small compared to the mass of these contaminants in the plume (Pilot Study Report, Appendix C, Section C.1.4). Thus "...scientists turned to the enhancement of microbial denitrification as a second option for plume nitrate (Pilot Study Report, p. 17)."

2.2.3 Natural Denitrification in the Alluvial Aquifer

Natural attenuation of nitrate in the alluvial aquifer was primarily controlled by microbial denitrification. This conclusion was based on the similarity of first-order denitrification rates in laboratory microcosms and those inferred from modeling of nitrate concentration trends in the alluvial aquifer (p. 27). The data and analyses on which this conclusion is based are reported in Carroll, et al. (2009) and summarized in the Pilot Study Report, Appendix C, Section C.2. This process would presumably apply to both the shallow and deep portions of the aquifer.

2.2.4 Enhanced Denitrification in the Alluvial Aquifer

Denitrification rates could be substantially increased by injecting a biodegradable organic substrate, such as ethanol, into the aquifer. This conclusion is based on the results of ethanol injection push-pull and natural gradient tests performed in the 2010 and 2011 pilot-scale field tests in the alluvial aquifer and on independent studies at other sites. This process would presumably apply to both the shallow and deep portions of the aquifer.

2.2.5 Remediation of Sulfate in Alluvial Aquifer

The rate of uptake of sulfate by phreatophytes was very small with respect to the (i) mass of sulfate in the plume, (ii) injection of ethanol into the aquifer reduced sulfate concentrations by producing hydrogen sulfide, and (iii) sulfate that would be sequestered in the soil using active phytoremediation. The latter two processes would presumably apply to both the shallow and deep portions of the aquifer.

2.2.6 Land-Farming Phytoremediation

Land-farming phytoremediation (pump and treat) would involve pumping water from the alluvial aquifer and applying it to plots of actively managed native phreatophytes. This remedial action could be applied to both the shallow and deep portions of the alluvial aquifer. DOE conducted field studies of the uptake of water, nitrate, and sulfate in irrigated plots of native phreatophytes (Pilot Study Report, Appendix E). Based on these studies, the Pilot Study Report concluded that the results "demonstrated that a land farm with a crop of native fourwing saltbush shrubs may work well as a backup remedy for the plume if other remedies prove to be insufficient." This conclusion assumes that plant transpiration and soil evaporation would be sufficient to consume the water pumped and that nitrate and sulfate would not be returned to the aquifer.

The rate at which water would need to be pumped from the alluvial aquifer to remove 90 percent of the plume mass in 30 years was estimated to be between 5.7 and 10.9 cubic meters per hour (m^3/hr) [21 and 40 gallons per minute (gpm)] in DOE (2000, Table 5-2). The Pilot Study Report also concludes that "Plant uptake and soil denitrification kept nitrate levels from building up in the land-farming soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum (calcium sulfate)..." (p. 28).

3 EVALUATION OF PILOT STUDY CONCLUSIONS

3.1 Subpile Soils

Based on the results of the preliminary and pilot studies, DOE made several conclusions about the likely success of remediation strategies for limiting future movement of ammonium (NH_4^+), nitrate (NO_3^{-1}), and sulfate (SO_4^{-2}) into the alluvial aquifer. DOE primarily concluded that (i) phytoremediation would consume water in the subpile soils, which would limit downward migration of ammonium, nitrate, and sulfate and (ii) natural and enhanced denitrification would reduce the nitrate content in the subpile soils by conversion of nitrate to either nitrous oxide (N_2O) or nitrogen gas (N_2). The following sections discuss the DOE conclusions in the Pilot Study Report.

3.1.1 Water Balance Using Enhanced Phytoremediation

DOE's conclusion that establishing healthy plants in subpile soils will reduce the downward migration of ammonium, nitrate, and sulfate in water during the growing season is valid based on the information evaluated in the Pilot Study Report. Establishing healthy vegetation will utilize available water in soils during the growing season, which will reduce the water content. The lower water content will significantly slow the downward water movement from the subpile soils toward the alluvial aquifer and slow the downward migration of ammonium, nitrate, and sulfate during the growing season. To establish healthy vegetative cover over the subpile soils, DOE transplanted fourwing saltbush and black greasewood, both native phreatophytes, to all fields. To support the transplants, drip irrigation was supplied as they grew. The amount of irrigation supplied was less than the amount that the plants could transpire. Because human involvement was needed for the transplanting and irrigation, DOE called these activities enhanced phytoremediation.

However during the nongrowing season, the water content of the subpile soils may increase to an amount that may induce flushing of ions (i.e., nitrate and sulfate) out of the subpile soils and downward toward the alluvial aquifer. For semi-arid sites, like the Monument Valley Site, water movement from soils to an underlying aquifer may occur from an unusually wet winter or quick and abundant snowmelt in the spring (Winograd, et al., 1998; Spangler and Johnson, 1999). During these events, the uptake of water by plants is significantly less than the amount of water being supplied. Consequently, the water content of the subpile soils may increase and result in downward water movement to the alluvial aquifer. Ions, such as nitrate and sulfate, will be transported with the water to the alluvial aquifer. Although a healthy vegetative community may utilize available water in soils during the growing season under average conditions (Scanlon, et al., 2005), nongrowing season precipitation may occur in which the plants cannot utilize all of the moisture and subsequent downward water movement may occur to underlying aquifers. In addition, cases may exist that groundwater recharge may occur at locations where the mean annual precipitation (i.e., water addition) is much less than the mean annual potential evapotranspiration as shown by Small (2005). Furthermore, Small (2005) states that mean annual precipitation and mean annual potential evapotranspiration alone are not good indicators to predict where groundwater recharge may occur. For a long-term remediation strategy, DOE needs to consider factors other than that the amount of water being supplied by precipitation and irrigation is less than the potential evapotranspiration. Potential effects of nongrowing season precipitation, and possibly episodic precipitation events, on the downward migration of ammonium, nitrate, and sulfate should be considered.

To monitor water content and potential downward water movement of the subpile soils in the pilot studies, DOE used a hydroprobe, water content reflectometers, and water flux meters. The hydroprobe measures soil water content by neutron thermalization. The water content reflectometers measure soil water content by electrical conductivity. The water flux meters measure water movement using a funnel, wick, and tipping bucket system where the collected water is weighed. Based on measurements of subpile soil water content and water flux, DOE concluded that enhanced phytoremediation successfully controlled the water balance of the subpile soils to limit downward water movement and the transport of ammonium, nitrate, and sulfate.

Questions remain regarding the conclusion by DOE of no downward water movement in the subpile soils including:(i) the water content deeper in the subpile soils for the Old Field appears to have an increasing trend, which may potentially result in downward water movement, especially if the trend continues; and (ii) only 4 water flux meters were used for the 3.3 ha [8.2 ac] of planted fields where enhanced phytoremediation was tested. For the former concern, Figure 3-1 shows an increasing trend of the soil water content at the 270–300 cm [106–118 inches (in)] depth. During the growing season of 2009 and 2010, it appears as if the volumetric water content exceeded the field capacity of 0.15 cm^3/cm^3 [15 percent] (Pilot Study Report, p. B–25). It is not clear why this increasing trend is only found in the Old Field. In a Groundwater Compliance Action Plan, DOE will need to give more detail on how irrigation will be managed to prevent an increase in water content deeper in the soil profile as shown in Figure 3-1. For the latter concern, data based on only 4 water flux meters for 3.3 ha [8.3 ac] may be insufficient to draw conclusions for all of the area. Only a single water flux meter was used on the Old Field. Because soils have heterogeneities in their structure, as do most natural porous media, downward water flux may be occurring at locations other than where the water flux meters are positioned.

It is reasonable to assume that during the growing season, established healthy plants can utilize available soil moisture and lower the water content of the soil. The result may be negligible downward water movement, or there may be no downward water movement to the underlying aquifer. However, there may be downward water movement to an aquifer if the amount of water being added to the soil is greater than the amount plants use during the nongrowing season or episodic precipitation events. Even if the average amount of water plants use is greater than the average amount of water being introduced to the soil, downward water movement may occur from nongrowing season precipitation, episodic precipitation events, and heterogeneities in soil properties and the distribution of roots. In a Groundwater Compliance Action Plan, DOE will need to address effects of nongrowing season precipitation and episodic precipitation events.

3.1.2 Enhanced Denitrification in the Vadose Zone

Based on measurements of nitrogen levels in the subpile soils early in the pilot studies, the decrease in nitrogen levels was significantly greater than what could be accounted for by the transplanted native phreatophytes extracting and metabolizing nitrogen and sulfur. DOE estimated that the transplanted shrubs in the Old Field removed only about 1 percent per year of nitrogen from the subpile soils over the 10-year period of the pilot studies. DOE concluded that denitrification by microorganisms was the likely cause for the measured reduction in nitrogen levels. It was assumed that the irrigation stimulated the microorganisms. Denitrification in soils is the biological reduction of nitrate to molecular nitrogen or nitrous oxide, which are both gases that can be released to the atmosphere. The microorganisms (bacteria)

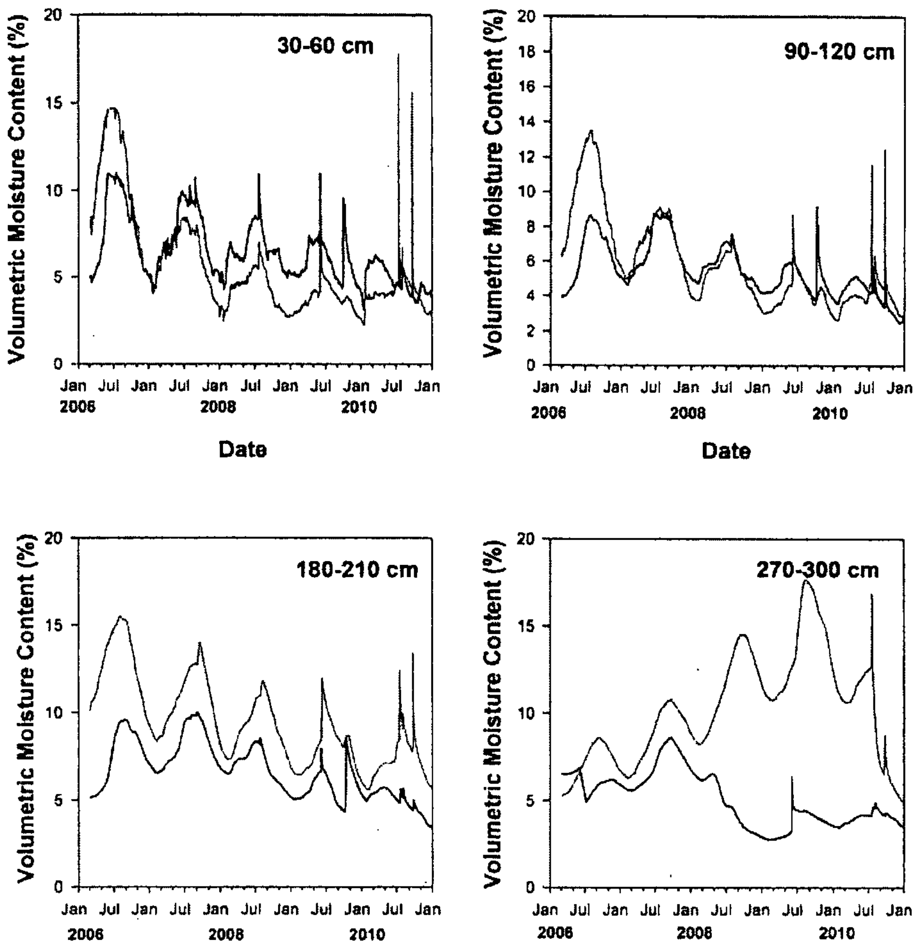

Figure 3-1. Soil Moisture Content at Four Soil Depths in Enhanced Phytoremediation Plots, Measured by Water Content Reflectometers. Results Are Daily Means of Water Content for Three Monitoring Stations in New Fields (Black Line) and One in the Old Field (Red Line). (Reproduced From the Pilot Study Report, Appendix B, Figure B–20).

generally responsible for denitrification obtain their energy by oxidizing a carbon source. It is generally reported that denitrification occurs under anaerobic conditions (Brady, 1974, p. 431; Hausenbuiller, 1972, p. 255). However, there have been published papers in which aerobic denitrification has been reported (Meiklejohn, 1940).

To verify that denitrification was contributing to the reduction in the measured nitrogen levels, assay chambers were placed over irrigated and nonirrigated subpile soils. The measured production of nitrous oxide was 10 to 20 times higher in assay chambers over the irrigated soils, indicating that (i) denitrification is occurring in subpile soils under aerobic conditions and (ii) the irrigation was enhancing the denitrification. In additional investigations, the ratio of ^{15}N to ^{14}N isotopes was measured because microorganisms are reported to prefer the ^{14}N isotope in their metabolism. It was found that the ratio increased over time, which supported the conclusion that denitrification was occurring because of an enrichment of ^{15}N. To further enhance denitrification, a carbon source (ethanol) was added to the irrigation water to support microbial growth. Whereas denitrification in laboratory studies increased when ethanol was added, denitrification was not further enhanced in the field investigation. Only under wet soil conditions did ethanol addition significantly enhance denitrification. It was concluded that irrigation would enhance denitrification, but the irrigation should be limited so as not to induce the downward migration of water (i.e., wet conditions). Over the 10 years of the pilot studies, DOE stated that irrigation-enhanced denitrification reduced the nitrogen levels in the subpile soils by approximately one half. It was noted that there was an initial rapid decrease in the early years with removal rates decreasing over time.

It is unclear whether the denitrification was occurring aerobically or occurring in small pockets or films with induced anaerobic conditions. Nevertheless, there was measured production of nitrous oxides, which indicates that denitrification was occurring in the subpile soils. For the water contents of the subpile soils during irrigation, well-aerated conditions should exist in most of the pore spaces. Any denitrification will lower the nitrate content of the subpile soils, provided that nitrification, which is the conversion of ammonium to nitrate by microorganisms, is not producing nitrate at a faster rate than is being reduced by denitrification. In the Pilot Study Report, DOE claimed that the nitrate produced from nitrification was then subject to denitrification, which resulted in a net loss of nitrogen from the subpile soils. However, Figure 3-2 shows that the loss of ammonium from the Old Field was greater than the loss of nitrate for the 10-year period of the pilot studies, except for the upper meter of the soil. The increase (negative loss in Figure 3-2) in nitrate at around the 4-m [13-ft] depth suggests that nitrate was added over time to this depth, which could have occurred from either (i) the downward movement of water and nitrate from above or (ii) by nitrification exceeding denitrification at this depth. The Pilot Study Report states that the irrigation enhanced denitrification. It is reasonable to assume that nitrification would not be similarly enhanced, but the Pilot Study Report does not explicitly address any enhancement of nitrification. The results shown in Figure 3-2 appear to contradict the results shown in Tables 3-1 and 3-2. The tables show that there was a greater reduction in nitrate than ammonium, but Figure 3-2 shows a greater reduction in ammonium. In Figure 3-3, the averages nitrate values for 2004 for each of the soil depths in Table 3-1 are plotted (broken lines). The results show that the nitrate levels in the upper part of the soil profile remain relatively unchanged between 2004 and 2010, but the nitrate levels in the lower part of the soil profile increase from 2004 to 2010. Further explanation from DOE may be required to clarify the overall effects of denitrification and nitrification on the nitrate and ammonium levels in the subpile soils and possible downward migration of nitrate in the subpile soil with time.

Denitrification and nitrification are components of the nitrogen cycle in soils. The biochemical conversion of nitrate to gaseous nitrous oxides and/or nitrogen gas (denitrification) is typically conducted by facultative anaerobic microorganisms (Brady, 1974, p. 431). The conversion of ammonium to nitrate (nitrification) is commonly facilitated by aerobic autotrophic bacteria that are ubiquitous in soils (Brady, 1974, p. 428). Only denitrification results in a loss of nitrogen (nitrate) from soils. Therefore, any enhancement of denitrification will result in a greater loss of nitrate than what would occur without the enhancement. Because nitrate is very mobile in soils, reduction in nitrate levels also will reduce the amount of nitrate that may potentially move downward toward an unconfined aquifer. In the Pilot Study Report, irrigation to enhance plant growth also serves to enhance microbial activity and consequently to increase the rate of denitrification. However, DOE has not demonstrated whether the enhancement of denitrification also enhances nitrification, which may result in more nitrate being created than is lost through denitrification. Furthermore, DOE has not demonstrated whether denitrification is a short term phenomenon or will continue for long periods. Data in Table 3-1 indicates that the reduction in nitrate occurred rapidly followed much slower reductions or even increases.

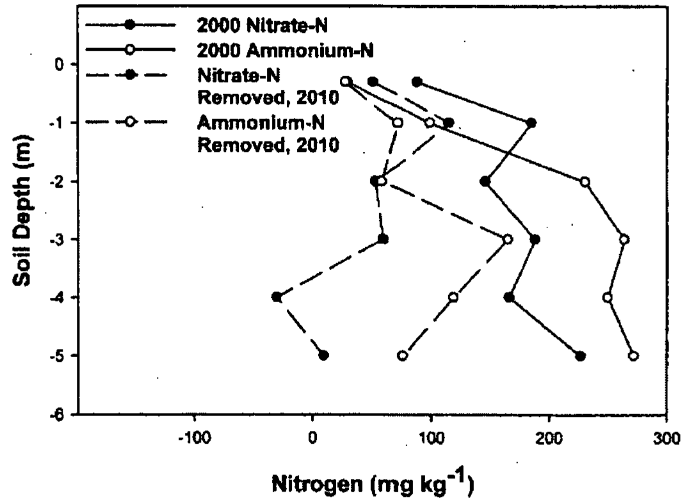

Figure 3-2. Initial Concentrations of Nitrate and Ammonium in the Old Field, 200, and the Amount of Nitrate and Ammonium Removed by 2010, As a Function of Soil Depth (Reproduced From the Pilot Study Report, Appendix B, Figure B–27).

3.1.3 Treatment of Sulfate in the Vadose Zone

In the Pilot Study Report, there were no investigations of processes minimizing the downward movement of sulfate to the alluvial aquifer other than controlling the water balance as discussed in Section 3.1.1. In fact, irrigating the subpile soils resulted in an increase of the sulfate content of the surface subpile soils, as shown in Figure 3-4, because the irrigation water contained sulfate. DOE did not address likely consequences of sulfate addition to the subpile soils if irrigation is used to enhance phytoremediation and denitrification. DOE indicated the possible formation of gypsum ($CaSO_4 \cdot 2H_2O$), but the process was not supported by measurements or analyses. Gypsum commonly develops in semi-arid soils, but this process typically occurs naturally over very long time periods (Hausenbuiller, 1972, p. 301). Gypsum may precipitate in soils when the solubility of the mineral is exceeded (Dixon and Weed, 1977, p. 84). In a Groundwater Compliance Action Plan, DOE may need to address the effects of any likely addition of sulfate to the subpile soils and support its assertions for the pH conditions that may prevail.

3.2 Alluvial Aquifer

3.2.1 Hydraulic Control Plume by Phreatophyte Evapotranspiration

The results of the pilot studies do not provide a sound basis for determining the rate at which or extent to which either existing or enhanced phreatophyte communities would remove water from the alluvial aquifer or slow the movement of the nitrate and sulfate plume. Based on the following considerations, the phreatophytes may be primarily removing water from the vadose zone before it reaches the alluvial aquifer rather than directly extracting it from the aquifer. First, the hydrogen and oxygen isotope analyses do not unambiguously support the conclusion

Table 3-1. Nitrate-N Concentrations (mg/kg) in Soil Samples From the Old Field, 2000 to 2004. The Field Is Divided Into Four Irrigation Zones That Were Each Samples at 2–5 Locations Near Neutron Hydroprobe Ports. Values Are Means With Standard Errors of Means in Parentheses. (Reproduced From the Pilot Study Report, Appendix B, Table B–2).

Zone/Depth (m)	2000	2001	2002	2004	Number of Samples
Zone 1					
0.3	71.8 (37.6)	100.8 (41.1)	22.6 (37.1)	25.9 (23.1)	5
0.9	90.6 (25.2)	31.2 (10.5)	7.0 (5.3)	42.9 (34.7)	5, 5, 5, 4
1.8	186.7 (73.9)	52.0 (21.1)	9.3 (6.1)	36.1 (28.8)	3, 3, 4, 4
2.7	218.0 (103.0)	77.5 (60.5)	10.9 (16.3)	27.8 (25.0)	2, 2, 2, 3
3.6	235.0	23.0	48.1		1
4.5	302.0	46.0	57.3		1
Zone 2					
0.3	92.8 (35.5)	112.6 (58.2)	44.1 (47.3)	61.6 (26.5)	5
0.9	154.4 (42.0)	44.0 (13.2)	51.1 (73.5)	39.7 (20.2)	5
1.8	111.2 (33.4)	69.8(34.3)	35.1 (24.1)	43.1 (36.4)	5
2.7	67.8 (24.6)	113.3 (35.8)	34.7 (22.1)	38.4 (29.7)	4, 4, 5, 4
3.6	77.0 (31.9)	90.7 (73.3)	49.5 (39.8)	61.5 (52.5)	3, 3, 3, 2
4.5	113.0 (12.0)	133.5 (35.5)	74.8 (10.8)	59.1 (17.3)	2, 2, 2, 4
Zone 3					
0.3	126.0 (34.3)	95.0(30.1)	73.4 (53.4)	92.9 (36.9)	5
0.9	276.5 (141.1)	116.0 (52.2)	82.6 (54.4)	60.9 (26.9)	5
1.8	213.2 (64.4)	146.2(58.2)	106.0 (41.2)	137.7 (72.3)	5
2.7	180.4 (65.3)	119.0 (53.6)	84.7 (62.1)	147.9 (75.5)	5
3.6	123.6 (35.7)	95.7 (27.9)	58.6 (48.7)	104.1 (39.6)	5, 4, 4, 5
4.5	170.3 (28.8)	164.7(108.8)	107.0 (76.3)	229.1 (111)	4, 3, 5, 4
Zone 4					
0.3	62.0 (13.8)	131.8 (40.9)	145.4 (104.5)	81.5 (55.3)	5
0.9	217.8 (138.4)	181.8(81.6)	74.9 (75.9)	122.6 (73.1)	5
1.8	173.4 (70.9)	170.8 (43.8)	88.2 (87.2)	134.5 (47.4)	5
2.7	286.6 (85.4)	185.6(55.6)	87.3 (97.1)	128.9 (39.9)	5
3.6	227.0 (118.8)	166.8(27.5)	312.7 (432.2)	156.7 (37.4)	5
4.5	322.6 (106.1)	240.8 (20.3)	283.8 (229.8)	181.6 (71.0)	5, 4, 5, 5
Average	164	116	82	91	

that the phreatophytes are directly transpiring water from the shallow aquifer. Figure 3-5 shows the correlation of enrichment of Hydrogen-2 (δD) versus Oxygen-18 (δ18O) in groundwater, phreatophyte stem moisture, and the vadose zone water. The phreatophyte stem moisture isotopic ratios all fall on the evaporated water line, as do the soil water ratios, indicating the stem water could be derived either from the vadose zone or locally recharged water.

Second, the evapotransipiration rates measured for both protected and unprotected stands of saltbush and black greasewood increase with annual precipitation, as illustrated in Figure 3-6. This suggests that the phreatophytes may be primarily removing infiltrating water before it recharges that aquifer. If the phreatophytes are primarily removing water from the saturated zone the evapotranspiration rates would not vary with annual precipitation. (Note: according to DOE, the water flux meters measured no downward water flux.)

To the extent that phreatophytes are removing water before it reaches the water table, they would be slowing groundwater flow and the movement of the plume. On the other hand, less uncontaminated water would infiltrate and reach the aquifer in areas outside of the subpile

Table 3-2. Ammonium-N Concentrations (mg/kg) in Soil Samples From the Old Field, 2000 to 2004. The Field Is Divided Into Four Irrigation Zones That Were Each Samples at 2–5 Locations Near Neutron Hydroprobe Ports. Values Are Means With Standard Errors of Means in Parentheses. (Reproduced From the Pilot Study Report, Appendix B, Table B–2).

Zone/Depth (m)	2000	2001	2002	2004	Number of Samples
Zone 1					
0.3	2.5 (1.2)	66.8 (53.5)	1.9 (0.83)	1.52 (0.51)	5
0.9	44.9 (45.5)	121.9 (62.1)	10.3 (11.1)	5.82 (3.98)	5, 5, 5, 4
1.8	102.7 (93.2)	146.7 (109.1)	57.8 (77.8)	85.3 (65.0)	3, 3, 4, 4
3.6	56.0	43.0	7.5		1
4.5	140.0	113.0	77.5		1
Zone 2					
0.3	8.2 (2.0)	55.3 (42.9)	12.3 (18.9)	1.37 (0.51)	5
0.9	155.2 (73.3)	110.8 (53.2)	93.3 (76.0)	74.6 (57.6)	5
1.8	329.6 (60.9)	200.2 (50.2)	196.1 (152.0)	191.5 (80.9)	5
2.7	287.0 (60.4)	226.1 (50.2)	257.0 (144.2)	230 (89)	4, 4, 5, 4
3.6	310.0 (60.4)	244.3 (22.6)	220.8 (141.2)	227.5 (62.5)	3, 3, 3, 2
4.5	360.0 (145.0)	349.5 (90.5)	290.0 (420.0)	251.7 (11.81)	2, 2, 2, 4
Zone 3					
0.3	109.6 (87.0)	116.1 (91.6)	131.4 (158.9)	95.8 (60.4)	5
0.9	183.2 (113.6)	257.7 (87.5)	270.8 (219.5)	186.0 (81.8)	5
1.8	397.6 (70.1)	258.9 (72.9)	332.0 (136.1)	205.1 (84.8)	5
2.7	340.4 (49.2)	360.3 (48.9)	400.0 (31.62)	286 (58.0)	5
3.6	432.1 (69.2)	380.3 (45.2)	410.0 (389.1)	307 (40.9)	5, 4, 4, 5
4.5	432.0 (105.0)	206.8 (84.2)	460.0 (159.4)	320 (113)	4, 3, 5, 4
Zone 4					
0.3	4.8 (1.2)	19.2 (5.0)	2.4 (1.8)	81.9 (79.5)	5
0.9	11.4 (9.6)	19.9 (10.1)	92.5 (178.8)	35.2 (19.7)	5
1.8	90.5 (54.3)	94.1 (70.0)	101.8 (199.1)	77.9 (74.3)	5
2.7	316.8 (167.0)	114.4 (100.8)	181.3 (221.6)	168.6 (108)	5
3.6	203.0 (118.8)	206.1 (103.6)	234.7 (278.4)	175.1 (103)	5
4.5	159.4 (103.7)	230.0 (90.4)	290.1 (278.5)	143.3 (120)	5, 4, 5, 5
Average	191	168	173	148	

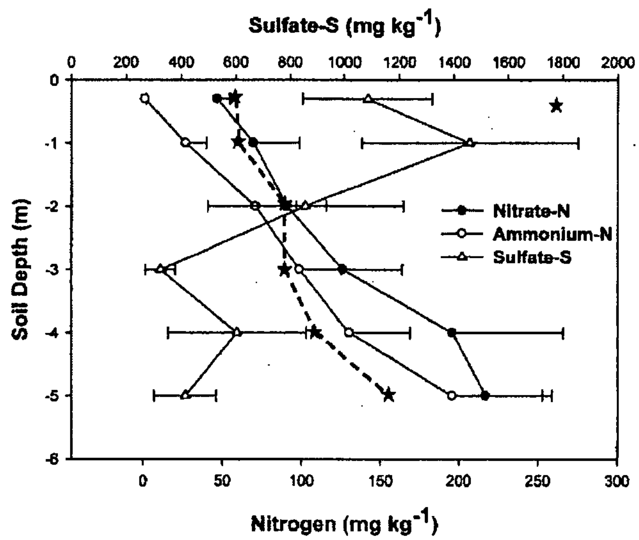

Figure 3-3. Distribution of Nitrate, Ammonium, and Sulfate as a Function of Soil Depth in Source Area Soil Samples From the Old Field in 2010 (Modified From the Pilot Study Report, Appendix B, Figure B–26)

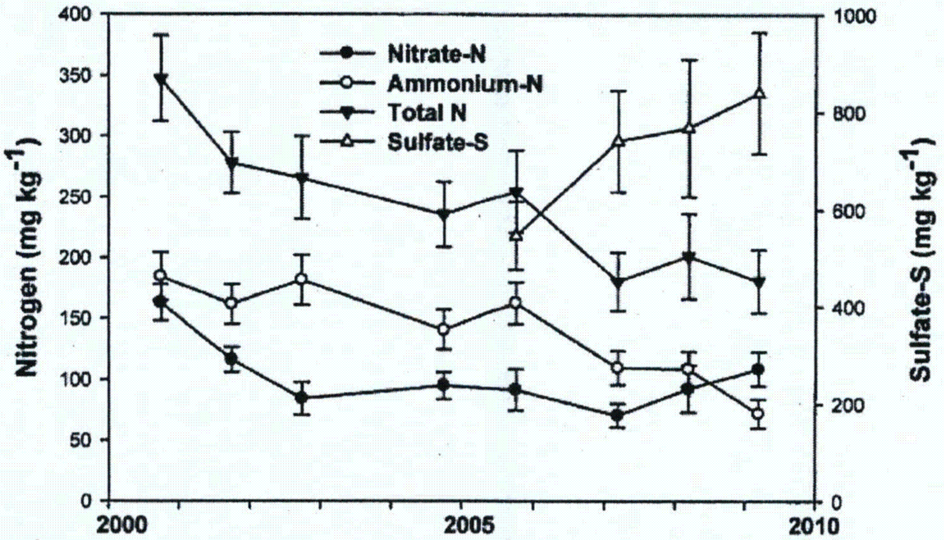

Figure 3-4. Concentrations of Nitrate, Ammonium, Nitrate + Ammonium (Total N), and Sulfate in Soil Samples From the Old Field, 2000 to 2010. Error Bars Are Standard Errors of Means. Sulfate Was First Measured in 2005. (Reproduced From the Pilot Study Report, Appendix B, Figure B–24)

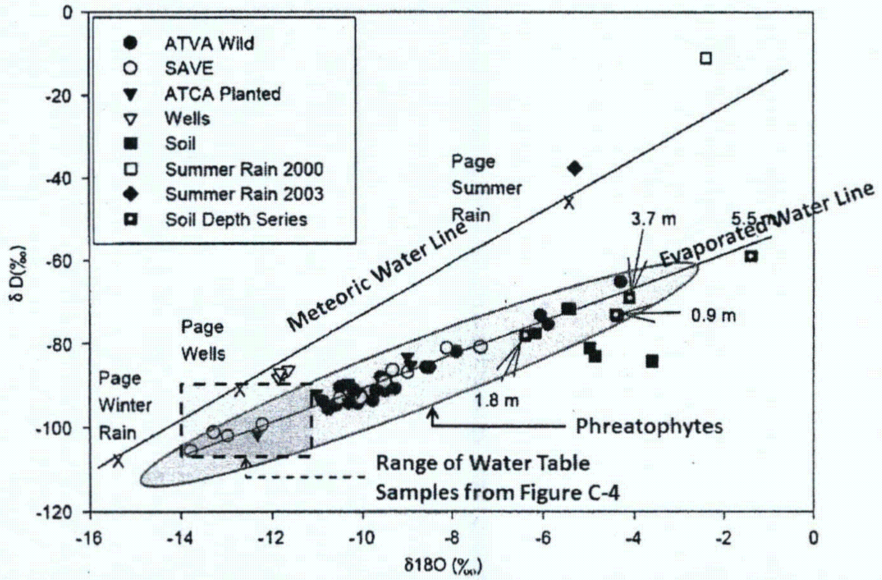

Figure 3-5. Correlation Between Hydrogen-2 ($\delta^{18}O$) Versus Oxygen-18 (δD) Enrichment in Phreatophyte Stem Moisture, Vadose Zone Soil Water, Rain Water at Page, Arizona and Well Water at Page, Arizona (Modified From Pilot Study Report, Figure C–2). The Phreatophyte Stem Moisture Isotopic Ratios All Fall on the Evaporated Water Line, as Do the Soil Water Ratios, Indicating the Stem Water Could Be Derived Either From the Vadose Zone or Locally Recharged Water. The Box Showing the Range of Water Table Samples Is Based on the Isotopic Data in the Pilot Study Report, Figure C–4 and the Water Table Elevations for Wells 607 and 677 (Reproduced From the Pilot Study Report, Appendix C, Figure C–2).

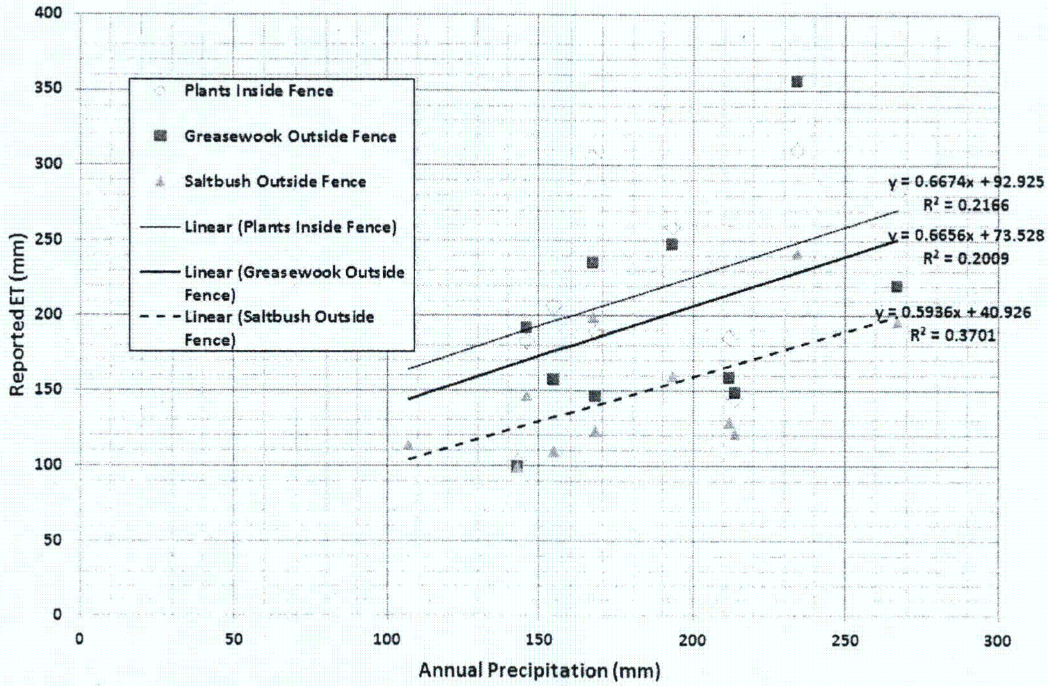

Figure 3-6. Correlation Between Reported Annual Evapotranspiration (ET) and Annual Precipitation for Protected Phreatophytes (Plants Inside Fence) and Unprotected Phreatophytes (Outside Fence)

source area to dilute contaminant concentrations outside of the subpile soil source area. With respect to the effects of revegetation and improved land management on hydraulic control of the plume, an increase in the total rate of evapotransipiration, whether taken from the vadose zone or the saturated zone, would undoubtedly slow the movement of the plume. However, as already stated, these effects would reduce dilution of nitrate and sulfate concentrations in the aquifer. If the phreatophytes are primarily removing water from the vadose zone, these effects will occur in both the shallow and deep aquifer zones. That the native phreatophytes are transpiring a substantial amount of water from the vadose zone is also implied by the results reported from land-farming pilot studies in the Pilot Study Report, Appendix E.

3.2.2 Phytoremediation of the Nitrate and Sulfate

The data on nitrate and sulfate uptake by phreatophytes from the alluvial aquifer in Section C.1.4 of the Pilot Study Report support DOE's conclusion that this mode of phytoremediation would not play a significant role in remediation of the alluvial aquifer.

3.2.3 Natural Denitrification in the Alluvial Aquifer

The Pilot Study Report relies on the close correspondence between denitrification rates measured in laboratory microcosms and those estimated from field nitrate concentration trends. The report concludes that microbial denitrification is the primary natural attenuation process in the alluvial aquifer. This conclusion is based on data from Carroll, et al. (2009). These data indicate that the denitrification rates estimated from field data only agree with the laboratory rates for the portion of the aquifer distal from the source area in which the dissolved oxygen concentrations are low (0.1 to 1.0 mg/L) [0.1 to 1 ppm] but denitrification rates are much lower closer to the source area where dissolved oxygen concentrations are higher. The decrease in dissolved oxygen concentrations is attributed to consumption of ammonia by microbial oxidation. Although the correspondence between the laboratory and field denitrification rates supports DOE's conclusion regarding the importance of microbial denitrification in the alluvial aquifer, sustaining the inferred denitrification rates is contingent on maintaining relatively low dissolved oxygen concentrations in the alluvial aquifer. This raises a question as to whether reducing or eliminating the source of ammonia to the alluvial aquifer in the subpile soil source area would increase the dissolved oxygen concentration in the aquifer and reduce the effectiveness of microbial denitrification in the pre-existing plume in the future.

3.2.4 Enhanced Denitrification in Alluvial Aquifer

The conclusion that denitrification rates can be increased by injecting a biodegradable, organic substrate into the aquifer is reasonable and consistent with findings from other sites. Enhanced denitrification occurs because microbial oxidation of the substrate reduces dissolved oxygen concentration to levels where microbial reduction of nitrate to reduced nitrogen species can occur. Enhanced denitrification also provides an organic nutrient to increase the microbial population. It remains to be determined whether enhanced denitrification of a large portion of the alluvial aquifer would be feasible due to the cost of adding an organic substrate and the complexity of controlling the movement and distribution of the organic substrate in the aquifer.

3.2.5 Remediation of Sulfate in Alluvial Aquifer

Except for the possibility of reducing sulfate concentrations by establishing reducing conditions through the injection of an organic substrate, as would be done for enhanced denitrification, the Pilot Study Report does not present any clear path forward for remediation of the sulfate plume, other than by reducing contributions from the subpile soils and land-farming phytoremediation. Normally, one would expect some natural attenuation of the plume as the result of physical dilution and mechanical dispersion in the aquifer if the source is eliminated. These processes would affect both the nitrate and sulfate plumes. If DOE's conclusion that microbial denitrification is the primary attenuation process for the nitrate plume, meaning that dilution and dispersion have negligible effects, then these physical attenuation processes would likewise have little effect on the sulfate plume.

3.2.6 Land-Farming Phytoremediation

The feasibility of using land-farming pump and treat to treat either the shallow or deep portions of the alluvial aquifer would depend on the ability of soil evaporation and phreatophyte transpiration to consume the water pumped from the aquifer and prevent nitrate and sulfate from leaching back into the aquifer. Nitrate leaching could also be prevented by the plants taking up the nitrate or by denitrification processes in the soil. Sulfate leaching could be prevented if the sulfate is sequestered in the soil in the form of a low solubility mineral, such as gypsum. The results of pilot studies presented in the Pilot Study Report, Appendix E found little or no nitrate accumulation in irrigated test plot soils, which DOE attributed to either plant uptake or leaching back into the aquifer [Note: DOE claims that there is no downward water movement in the subpile soils (Pilot Study Report, Appendix E, p. E–9)]. The black greasewood plots were found to have lower evapotranspiration rates than the fourwing saltbushplots because nitrate and sulfate leaching occurred in these plots (Pilot Study Report, Appendix E, p. E–0).

An important question that the Pilot Study Report leaves unanswered is the area of land farming that would be required to evapotranspire the pumped water. DOE (2000) estimated that the pump and treat alternative would require pumping 4.8 to 9.2 m^3/hr [21 to 40 gpm] of water from the alluvial aquifer. These rates imply that between 4.2×10^4 and 7.9×10^4 m^3 [1.5×10^6 and 2.8×10^6 cubic feet (ft^3)] per year of water would need to be evapotranspired. Based on data presented in the Pilot Study Report, Appendix C, the average actual evapotranspiration rate for phreatophytes at the site was approximately 200 millimeters (mm) per year [0.66 ft/year]. This evapotranspiration rate implies that a minimum of 21.4 to 25.9 ha [53 to 64 ac] would be required to consume all of the pumped water, ignoring natural precipitation. As discussed previously, estimated annual evapotranspiration rates on test plots were comparable to annual precipitation, so the area needed to evapotranspire both the pumped water and precipitation would likely be greater. The Pilot Study Report does not analyze whether the area available for land farming is sufficient to consume the water from the pumping system.

3.3 Contribution of the Final Pilot Study Report to Obtaining the Objectives As Stated in the Work Plan

Table 3-3 lists the extent to which the Pilot Study Report addresses the objectives and scope for pilot studies presented in the Work Plan (DOE, 2005).

Table 3-3. Objectives and Scope for Pilot Studies in the Work Plan

Work Plan Objective	Extent Addressed in Pilot Study Report
Delineate extent of nitrate, ammonium, and sulfate in subpile soils	DOE delineated the extent of these contaminants (Appendix B)
Investigate presence and mobility of natural nitrate and sulfate sources	DOE found natural nitrate to be indistinguishable from plume nitrate, and natural sulfate to be present, but not significant, with respect to sulfate from the milling process (Appendix B)
Determine causes of stunted plant growth and recourse	Results of soil sampling and greenhouse studies provided clues as to the causes of stunted growth, but an effective remedy was not found.
Expand irrigated planting of Atriplex canescens [four-wing saltbush]	DOE established irrigated test plots, but these plots are of limited extent
Quantify effects of irrigation on microbial denitrification processes and rates	DOE found that increasing the water content of the vadose zone soils increases the denitrification rate. Adding an organic substrate (ethanol) to the irrigation water of the field test plots did not substantially increase denitrification rates. Assessing nitrate concentrations with time in irrigated and non-irrigated plots provided a measure of effects of irrigation on microbial denitrification in subpile soils.
Investigate nitrification processes, rates, and possible enhancements.	DOE focused primarily on denitrification. No attempts were made to directly enhance nitrification. The loss of ammonium was attributed to nitrification, and the nitrate produced was subject to denitrification.

3.4 Contribution of the Final Pilot Study Report to Achieving the Objectives As Stated in the Pilot Study Report

Table 3-4 lists the extent to which the pilot studies contribute to achieving the objectives as stated in the Pilot Study Report.

Table 3-4. Contributions to Achieving Objectives of the Final Pilot Study

Pilot Study Objective	Extent Achieved
Estimate the total capacity of natural chemical and biological processes that are reducing concentrations of groundwater contaminants at the site	Although the investigation results reported in the Pilot Study Report provide information on the processes and rates of natural attenuation of nitrate, ammonium, and sulfate, the Pilot Study Report does not quantify the total attenuation capacity of the processes.
Investigate methods to enhance and sustain attenuation processes that could be implemented if the total capacity of natural processes is inadequate	The pilot studies found that conversion of ammonium to nitrate and denitrification in the vadose zone could be enhanced by increasing the water content of the vadose zone and adding an organic substrate. The pilot study found that denitrification rates in the aquifer could be increased and sulfate concentrations decreased by adding an organic substrate.
Demonstrate methods for (i) characterizing attenuation rates, (ii) verifying short-term results, and (iii) monitoring performance of natural attenuation processes and enhancements.	The pilot studies demonstrated that denitrification rates could be characterized through a combination of field and laboratory studies, the use of stable nitrogen isotope ratios, and field monitoring of concentrations.
Evaluate land farming as an active remediation option if natural and enhanced attenuation processes are both inadequate	The pilot study report evaluated evapotranspiration rates of protected and unprotected plots of phreatophytes and the effects of irrigation on phreatophyte growth and soil moisture profiles. The pilot study report did not quantify the irrigated area that would be required for land farming water pumped from the aquifer or extent to which contaminants in the irrigation water would be removed or sequestered.

4 RECOMMENDATIONS

4.1 Subpile Soils

4.1.1 Water Balance Using Enhanced Phytoremediation

DOE intends to use enhanced phytoremediation to control the water balance of the subpile soils so that ammonium, nitrate, and sulfate will not be a source of contamination in the alluvial aquifer. For this approach to be effective, DOE needs to consider effects of nongrowing season precipitation and episodic precipitation events on the potential downward migration of ammonium, nitrate, and sulfate. Episodic flow in arid to semi-arid climates can occur in response to a sequence of precipitation events (Scanlon, et al., 1997). Summer monsoonal rains may be a source for episodic precipitation events, as well as El Niño, Pacific decadal oscillations, and larger scale weather patterns. In its argument supporting enhanced phytoremediation, DOE neglected any effects of nongrowing season precipitation and episodic precipitation events that may supply sufficient water to the subpile soils and would result in leaching of ammonium, nitrate, and sulfate toward the alluvial aquifer. Although episodic events and abundant nongrowing season precipitation are not common, they can be a major cause for groundwater recharge from overlying soils in semi-arid climates (Spangler and Johnson, 1999). As reported by the Western Regional Climate Center in Reno, Nevada, the monthly total snowfall in December 1992 was 114 cm [45 in] (http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?azmonu, monthly snowfall listings), which could be considered an episodic event that could generate groundwater recharge.

In addition, DOE needs to provide further evidence that there is no downward water migration. Other than measurements of water content, there was only a single water flux meter in a 1.7-ha [4.2-ac] field (the Old Field). A single water flux meter is not sufficient to conclude that there is no downward water movement from subpile soils toward the alluvial aquifer. Further, DOE should explain why the water content at the 270–300 cm [106–118 in] depth appears to have an increasing trend, which may indicate downward water movement.

4.1.2 Enhanced Denitrification in the Vadose Zone

DOE plans to supply irrigation water to support phytoremediation as was conducted in the pilot studies. The resulting higher water content in the subpile soils may enhance denitrification over what would occur under drier conditions. In the pilot studies, there was an initial rapid decrease in nitrate levels followed by slower reductions. Based on the observed trend that there appears to be only very minor reduction in nitrate levels between 2004 and 2010 in the subpile soil (Figure 3-3), DOE needs to estimate what the consequences may be from long-term irrigation and what effect enhanced nitrification, in addition to enhanced denitrification, may have on nitrate levels in the subsoils.

In addition, DOE needs to resolve the apparent contradiction between Tables 3-1 and 3-2 and Figure 3-2. In the tables, more nitrate appears to have been removed than ammonium. In the figure, more ammonium appears to have been reduced than nitrate. The increase in nitrate deeper in the subpile soil between 2004 and 2010 also needs to be clearly explained.

4.1.3 Sulfate in the Vadose Zone

In Figure 3-3, DOE shows that the sulfate concentration in the subpile soils increased because the irrigation source contained sulfate. DOE did not address directly how this increase may affect the subpile soils and potential remediation activities over a long time period. The consequence of adding sulfate to the subpile soils, especially if long-term irrigation is proposed, will need to be investigated.

4.2 Alluvial Aquifer

The following sections contain recommendations specifically related to remediation of the alluvial aquifer.

4.2.1 Hydraulic Control of Plume by Phreatophytes

The Pilot Study Report does not provide clear estimates of how much water an enhanced population of phreatophytes would withdraw directly from the shallow alluvial aquifer versus the amount they would withdraw from the vadose zone. DOE should provide such an estimate and supporting calculations of the rate of groundwater movement to determine how an enhanced population of phreatophytes would affect the movement of the contaminant plume in both the shallow and deep portions of the aquifer.

4.2.1 Phytoremediation of the Nitrate and Sulfate

Because the Pilot Study Report found that the rate of uptake of nitrate and sulfate by phreatophytes from the alluvial aquifer was very small with respect to the mass of these contaminants in the aquifer, no recommendations are made to further investigate this remedial process.

4.2.2 Natural Denitrification of the Alluvial Aquifer

The Pilot Study Report and supporting data indicate that natural denitrification is occurring primarily in the portion of the alluvial aquifer downgradient from the subpile soils where the dissolved oxygen concentration in the groundwater is conducive to denitrification. This zone of depleted dissolved oxygen is probably the result of aerobic nitrification of ammonium near the subpile soil source area. If phytoremediation of the subpile soil area successfully reduces the ammonium load to the aquifer, the dissolved oxygen content in the aquifer may increase and reduce the effectiveness of denitrification in the alluvial aquifer. Although reducing the ammonium load to the aquifer from the subpile soil area is desirable for reducing the contribution of nitrate to the aquifer, DOE should evaluate how this might affect natural attenuation of the downgradient portion of the nitrate plume given the relatively low importance attributed to physical attenuation processes (dilution and dispersion).

4.2.3 Enhanced Denitrification of the Alluvial Aquifer

The results of pilot studies indicate that adding a carbon substrate, such as ethanol, can increase denitrification in the alluvial aquifer. Enhanced denitrification was also found to reduce sulfate concentrations, presumably by reducing sulfate to sulfide. If this action is selected in the Groundwater Corrective Action Plan, additional studies would be required to determine the technological and economic feasibility of large-scale injection of organic chemicals into the aquifer, as well as an evaluation of any secondary deleterious effects on water quality.

4.2.4 Remediation of Sulfate in the Alluvial Aquifer

Assuming that physical natural attenuation processes play a limited role in attenuating nitrate in the alluvial aquifer, they would also play a limited role in remediation of the sulfate plume. The only actions for remediation of the sulfate plume the pilot study addressed were pumping water from the aquifer and irrigating fields of phreatophytes, or enhanced denitrification, that also reduced sulfate concentrations. Additional investigations would be required to determine the capacity of the shallow soils and vadose zone to sequester sulfate in some relatively immobile form. If, as DOE hypothesized, the sulfate applied to the land-farming area is sequestered as gypsum ($CaSO_4 \cdot 2H_2O$), then any water infiltrating the land-farming area exceeding what is transpired will have a sulfate concentration determined by the solubility of gypsum. In the simplest case, the sulfate concentration in the infiltrating water can be estimated from the solubility of gypsum determined by

$$\frac{C_{Ca}}{M_{wCa}} \frac{C_{SO4}}{M_{wSO4}} = K_{sp} = 6.1 \times 10^{-5} \tag{4-1}$$

Where

C_{Ca}	–	Concentration of calcium ions in grams per liter [g/L]
C_{SO4}	–	Concentration of sulfate ions in [g/L]
M_{wCa}	–	Molecular weight of calcium in grams per mol [g/mol]
M_{wSO4}	–	Molecular weight of sulfate in [g/mol]
K_{sp}	–	Solubility product of gypsum in mol^2 per liter^2 [mol^2/L^2]

As indicated, the solubility product of gypsum is approximately 6.1×10^{-5} mol^2/L^2 (Skoog and West, 1974). Assuming that calcium concentration is approximately equal to the sulfate concentration, the solubility product equation can be rearranged to solve for the sulfate concentrations as

$$C_{SO4} = \sqrt{6.1 \times 10^{-5} \times 40\frac{g}{mol} \times 96\frac{g}{mol}} = 0.48\frac{gm}{L} \equiv 480\frac{mg}{L}[ppm] \tag{4-2}$$

Based on this calculation, the sulfate concentration in the infiltrating water could exceed the Navajo Nation goal for remediation of sulfate of 250 mg/L [250 ppm] unless it is attenuated by other mineral or ion exchange reactions. Additional studies are needed to determine the ultimate capacity of the soil and vadose zone in the potential land-farming areas to sequester sulfate so that it does not return to the aquifer at concentrations that would exceed the Navajo Nation goal for remediation of sulfate.

4.2.5 Land-Farming Phytoremediation

The land-farming pump and treat alternative will require that the land-farming area be sufficient to completely evapotranspire the applied groundwater plus natural precipitation. DOE should provide an estimate of the land-farming area that would be required to manage the pumped groundwater that accounts for a limited growing period and natural precipitation at the site, including the effect of unusually wet years and extreme precipitation events.

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